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13. ABSTRACT (Maximum 200 words)

This report summarizes presentations, discussions and conclusions from the Workshop, "Microchemical Systems and Their Applications," held June 16-18, 1999, in Reston,Virginia USA. The objectives were to establish: (i) for which application areas microreactors would have potential, (ii) essential scientific problems that would have to be solved to realize particular devices, and (iii) the time scale for developing microreactor technologies. The workshop also reviewed fabrication techniques beyond standard silicon based MEMS processes and incorporating metals, polymer, and ceramics. The workshop participants reflected the multidisciplinary nature of microchemical system research and represented government, industry and university organizations. The format consisted of invited talks reviewing the state-of-the-art in microchemical systems, application needs, and relevant fabrication issues. These issues were further elaborated upon in a poster session. The presentations and posters were followed by three breakout sessions addressing specific objectives of the workshop, specifically (1) Opportunities for microenergy devices, (2) Challenges and needs in microfabrication and materials, and (3) Chemical applications of microchemical systems. Promising applications of microreaction technology were identified along with needs for microreaction technology research and development. The report contains of an executive summary, background information, summaries from the working group, and copies of presentations and posters.

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Microchemical Systems and Their Applications

Workshop held June 16-18 1999

Reston,Virginia USA

Sponsored by

Army Research Office (ARO) and

Defense Advanced Research Projects Agency (DARPA)

1. Abstract

This report summarizes presentations, discussions and conclusions from the Workshop, "Microchemical Systems and Their Applications," held June 16-18, 1999, in Reston,Virginia USA. The objectives were to establish: (i) for which application areas microreactors would have potential, (ii) essential scientific problems that would have to be solved to realize particular devices, and (iii) the time scale for developing microreactor technologies. The workshop also reviewed fabrication techniques beyond standard silicon based MEMS processes and incorporating metals, polymer, and ceramics. The workshop participants reflected the multidisciplinary nature of microchemical system research and represented government, industry and university organizations. The format consisted of invited talks reviewing the state-of-the-art in microchemical systems, application needs, and relevant fabrication issues. These issues were further elaborated upon in a poster session. The presentations and posters were followed by three breakout sessions addressing specific objectives of the workshop, specifically (1) Opportunities for microenergy devices, (2) Challenges and needs in microfabrication and materials, and (3) Chemical applications of microchemical systems. Promising applications of microreaction technology were identified along with needs for microreaction technology research and development. The report contains of an executive summary, background information, summaries from the working group, and copies of presentations and posters.

1.1 Organizing Committee:

Peter Fedkiw, North Carolina State University/ARO

Klavs F. Jensen, MIT

Robert Nowak, DARPA/DSO

Richard Paur, ARO

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2. Executive Summary

2.1 Introduction

Microfabrication techniques and scale-up by replication have fueled spectacular advances in the electronics industry, and they have started to revolutionize biological research and drug discovery. Microfabrication offers a similar potential for faster, cheaper, better chemical product research and development and, possibly, product production. Microchemical systems have feature sizes in the micron to hundreds of micron range, and reaction components are integrated with miniaturized sensors and actuators. The reduction in size and integration of multiple functions create structures with capabilities that exceed those of conventional macroscopic systems and add new functionality.

These developments build, in part, on advances in MicroElectroMechanical Systems (MEMS)[1]; a field that started by using fabrication techniques developed for microelectronics to construct sensors and actuators, but now encompasses a wide range of materials and microfabrication methods. MEMS devices are now found in a wide range of automotive, aircraft, health care, printing, and optical applications. The research investment made in MEMS has enabled the fabrication of microchemical reaction systems. Many of the components (*e.g.*, valves, pumps, flow sensors, mixers, and separation devices) needed in integrated chemical systems have been demonstrated in a wide range of metals, ceramics, and polymers.[2] Miniaturization of chemical analytic devices in "micro-total-analysis-systems" (μTAS)[3] represents a natural extension of MEMS technology to chemistry and biology with obvious application in combinatorial chemistry, high throughput screening, and portable analytical measurement devices.

Microfabricated chemical devices have advantages in terms of portability, flexibility, and ease of integration with sensor and actuators. However, it is not yet understood which applications would benefit most from new micro (or meso) chemical approaches and to what extent such methodologies would be feasible within the next five years. Thus, there is a need to establish the state-of-the-art in microfabricated chemical systems, potential applications, limitations of the technology, and strategies for evolving microchemical systems.

2.2 Workshop Objectives

The objective of the workshop was to review the state-of-the-art in microchemical systems, with emphasis on microreactor systems for chemical applications such as power generation, portable air purification, and chemical synthesis. Miniaturization of analytical devices, μTAS, and biological applications, such as detection and cell-based systems, offer exciting opportunities

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[1] K. D. Wise, "Special Issue on Integrated Sensors, Microactuators, and Microsystems (MEMS), *Proceedings of the IEEE* 1998, *86*, 1531-1533.

[2] W. Ehrfeld, V. Hessel and H. Lehr, "Microreactors for chemical synthesis and biotechnology–Current developments and future applications," *Topics in Current Chemistry* ("Microsystem Technology in Chemistry and Life Science") 1998 *194*, 233-252, Springer Berlin.

[3] van den Berg, A. and D. J. Harrison (Eds.), *Micro Total Analysis Systems'98*, Kluwer Academic Publishers, Dordrecht (1998).

worthy of workshops dedicated specifically to those topics and thus were not included in the workshop.

The objectives were to establish: (i) for which application areas microreactors would have potential, (ii) essential scientific problems that would have to be solved to realize particular devices, and (iii) the time scale for developing microreactor technologies. An important aspect of this effort was to identify limits to the technology and areas in which microchemical systems would not be useful. The workshop also reviewed fabrication techniques beyond standard silicon based MEMS processes would incorporate metals, polymer, and ceramics.

The workshop participants reflected the multidisciplinary nature of microchemical system research and represented government, industry and university organizations. In order to include significant developments in the field overseas, in particular in Germany, a few international experts were also invited. The format consisted of invited talks reviewing the state-of-the-art in microchemical systems, application needs, and relevant fabrication issues. These issues were further elaborated upon in a poster session. The presentations and posters were followed by three breakout sessions addressing specific objectives of the workshop, specifically:

1. Opportunities for microenergy devices
2. Challenges and needs in microfabrication and materials
3. Chemical applications of microchemical systems

2.3 Recommendations of the Working Groups

Working Group 1 identified features of microchemical systems that make them potentially highly relevant in small power generation devices. Since chemical fuels possess energy densities two orders of magnitude higher than rechargeable batteries, application of microchemical devices in fuel processing for power generation could result in much higher energy densities than batteries. The power generation applications envisioned for microchemical systems are those which can most benefit from the assumed improvement in energy density. Examples include portable power, remote/off-grid power generation, stationary rechargers, camping, robotics, guided munitions, distributed sensing systems, and backup power. Two power generation approaches were considered: (i) a fuel reformer combined with a fuel cell and (ii) combustion, combined with thermoelectric elements, thermophotovoltaics, or thermal cycle engines.

Development of microchemical power generation systems represents a departure from traditional engineering approaches. The small scales of the devices dramatically changes the heat and mass transport properties, increases the importance of surfaces, and generates a novel set of engineering problems which do not apply for conventional scale equipment. Fast heat transport can be advantageous, but it can also be highly undesirable from the standpoint of heat losses. Micro/meso fabrication methods may eventually produce ultra compact equipment usually thought of as peripheral, such as pumps, valves, fans, and filters. The overall system performance (efficiency, reliability) will depend much more directly on these micro-peripherals than in large chemical processing systems. High processing temperatures also dictate the use of high temperature materials, and appropriate fabrication methods must be devised to integrate these materials. Novel thermal insulating materials and thermal device designs must be pursued. Micro and meso fabrication approaches need to be extended to enable more flexible device

design and integration of catalysts, adsorbents, insulators, and high temperature materials. The fuel dictates the processing needs, and although diesel fuels are desirable, the simple, single chemical fuels offer advantages in terms of processing demands, purity, and fouling that could make the difference for technology feasibility.

The requirements for specific applications drive the need to extend existing techniques for microfabrication and to produce microstructures in materials other than silicon. Applications in the area of microchemical systems that Working Group 2 considered, were devices for chemical synthesis, systems for power generation, total microanalysis systems, and devices for environmental remediation. Challenges in fabricating these types of microchemical systems arise because of various practical constraints: the devices may need to withstand extremes in temperature, high pressures, and harsh chemical conditions. These requirements must be met while components that perform multiple functions are integrated, precision in fabrication is maintained, and an appropriate packaging solution is developed. All of these needs must be met within a reasonable period of time and at a tolerable cost.

Two issues in the discussion of the fabrication of microchemical devices were recurrent: (i) the design of systems that incorporate different materials and (ii) packaging of microchemical devices. If it is going to be possible to incorporate different materials into microchemical devices, then it is essential that methods for integrating and bonding dissimilar materials be developed. Currently, lamination of patterned sheets is the dominant method for bonding complex microstructures. While there is no general solution to the bonding problem, it is a critical area for improvements in the fabrication of miniaturized devices. The other issue that is relevant to all systems is the question of packaging: should fabrication be integrated or modular? The consensus was that a modular approach would be more flexible.

Several recommendations were made for the development of an infrastructure that would facilitate the accessibility of the technology for producing microfluidic/microchemical systems; in particular, a foundry for microfabricate devices, standardization of both fluidic and electrical interfaces, and the creation of design rules for devices. A database of materials properties also should be established.

The third Working Group assessed chemical applications of microreaction technology. Specific opportunities were discussed along with research needs and barriers to implementation. The integration of sensors (flow, pressure, temperature and chemical species) and actuators (heaters and valves) with reaction channels was deemed desirable, but not necessary, for a device to be a microchemical system. Microreaction technology should not be viewed as a means for miniaturization of existing processes, but rather for realizing new processes under more aggressive, better contacting conditions, where reaction rates and product yields are higher than in standard reaction equipment. The group identified a number of additional applications for different chemical industry segments:

- Fuels and energy
- Laboratory and pilot plant instrumentation
- Biochemical processing
- Pharmaceutical and fine chemical production
- Sustainable development - environmental friendly production.

- Personal care and cosmetic products
- Devices for medical diagnostics

Advances in microreaction technology will require multidisciplinary research approaches. Research must be done in relevant areas of transport phenomena, chemistry, materials, and fabrication technology to realize the promise of microreaction technology. Description of microchemical device performance must be based upon a systems approach that integrates chemical, transport, mechanical, and electrical components along with an economic analysis. Models must also reflect the multiple length and time scales involved in microreaction technology. It will also be essential to understand process transients and to integrate process control in the early stages of microreactor design considerations. The packaging of multiple reactors presents significant challenges in fluid handling, local reactor monitoring and control not previously addressed in traditional design of chemical plants. Answering the question: "when is smaller better?" should be central to the development of any microreactor system.

Industrial acceptance of microreaction technology will ultimately depend on (i) demonstrated applications examples, (ii) exposure of the technology to decision makers, (iii) the availability of packaged devices easily integrated into chemical laboratories, (iv) development of fabrication infrastructure (foundries and engineering)), and (v) development of standards for integration and fabrication. Research and development of microreaction technology will be enhanced by educational initiatives; specifically interdisciplinary courses, training of process personnel, and development of reviews and texts on all aspects of microchemical reaction technology.

3. Presentations and Schedule

Wednesday June 16

5:00pm - 6:45pm:	Registration and reception	
7:00pm - 7:20pm:	Welcome, DoD R&D focus	Dick Paur/Peter Fedkiw ARO Robert Nowak DARPA/DSO
	Workshop organization and objectives	Klavs Jensen/MIT

3.1 Plenary session: Microchemical Systems and Applications

Moderator: Klavs Jensen, MIT

7:20 pm - 8:00 pm	Wolfgang Ehrfeld Institute for Microfabrication, Mainz, Germany

8:00 pm - 8:40 pm	Integrated Reaction, Separation, and Detection Systems for Biochemical Analysis	Mark Burns University of Michigan
8:40 pm - 9:20 pm	Recent Results of Chemical Syntheses on a Microfluidic Chip	Rolf E. Swenson Orchid Biocomputer
9:20 pm - 10:00 pm	Gas Phase Chemical Detection with and Integrated Chemical Analysis System	Steve Casalnuovo Sandia National Laboratories

Thursday June17

3.2 Plenary Session: Chemical and Fuel Processing -

Moderator: Peter Fedkiw, NCSU/ARO

8:00am - 8:40am	Microchemical System Applications - DuPont Experience	Jim Ryley, DuPont Experimental Station
8:40am - 9:20am	Hydrocarbon Fuel Processors - Development Issues in Fuel Cell Vehicle Applications	Richard Bellows, Exxon Research and Engineering
9:20am - 10:00am	Fuel Processing in Microchannel Reactors.	Anna-Lee Tonkovich Pacific Northwest National Laboratory

10:00am - 10:30am Break

Plenary Session: Chemical and Fuel Processing (continued)

Moderator: Dick Paur, ARO

10:30am - 11:10 am	Catalytic Partial Oxidation at Millisecond Times	Lanny Schmidt University of Minnesota
11:10am - 11:50 am	Combustors for Micro Heat Engines	Ian Waitz, MIT
11:50am - 12:30 am	Man-portable Microtechnology Based Absorption Heat Pump.	Michele Friedrich Pacific Northwest National Laboratory

12:30pm - 1:30pm: Lunch

3.3 Plenary Session: Materials and Microfabrication

Moderator: James F. Ryley, DuPont

1:30pm - 2:20 pm	Microfabrication and Microfluidics Using Polymers and Rapid Prototyping	George Whitesides, Harvard University
2:20pm - 3:00 pm	Novel MEMS fabrication approaches (tentative title)	Martin A. Schmidt MIT
3:00pm - 3:40 pm	Microfluidic Systems Fabricated in Low Temperature Co-fired Ceramic Tapes	Haim H. Bau University of Pennsylvania

3:30pm - 6:00pm: Coffee Break, **Poster Session**, and Informal Discussions

6:00pm - 7:00pm: Initial Meeting of Working Groups:

I: *Opportunities for Microenergy Devices,* Moderator: Robert Wegeng, PNNL

II: *Challenges and Needs in Microfabrication and Materials,* Moderator: Martin Schmidt, MIT

III: *Chemical Applications of Microchemical Systems*, Moderator: Klavs Jensen, MIT

7:00pm - 8:30 pm: Dinner, Ballrooms B&C

Speaker: Lawrence H. Dubois, DARPA/DSO "Mesoscopic Machines - There is plenty of room in the middle!"

Friday June 18

3.4 Working Groups

8:00am - 12:30pm:

I: *Opportunities for Microenergy Devices,* Moderator: Robert Wegeng, PNNL

II: *Challenges and Needs in Microfabrication and Materials,* Moderator: Martin Schmidt, MIT

III: *Chemical Applications of Microchemical Systems*, Moderator: Klavs Jensen, MIT

12:30pm - 2:00pm: Lunch

2:00pm - 3:30pm:	Plenary session - Summaries
3:30pm:	Adjourn

3.5 Poster Session

Presenter	Title
Jeffrey G. Killian Johns Hopkins University	Developing Conducting Polymers for Charge Storage Applications
Brian K. Paul Oregon State University	Microlamination for Microtechnology-Based Energy and Chemical Systems
Xiang Zhang Pennsylvania State University	Microfabrication of Truly 3D Complex Microstructures with Materials Beyond 1C Processes
L. James Lee Ohio State University	Fabrication Techniques for Polymer Based Microfluidic Devices
Debra R. Rolison Naval Research Laboratory	Using Nanoscale Mesoporous Architectures to Design Integrated Fuel Cell Catalysts or Pave High Surface Areas with Nanowires
John N. Harb, Brigham Young University	Microbatteries for Use with MEMS Devices
Mark R. Holl University of Washington	A Microfluidic Sample Preconditioning System for CBW Agent Detection and Quantification
Nitish V. Thakor Johns Hopkins University	VLSI Electrochemical Sense Array for Chem/Bio/Neuro
Anil R. Oroskar UOP	Process Intensification Needs in Petroleum & Petrochemical Industry
Eduardo E. Wolf University of Notre Dame	Microfabricated Bimetallic Catalysts for the Hydrogenation of Croton Aldehyde

Goran Jovanovic Oregon State University	A Microtechnology Based Chemical Reactor System for Catalytic Dechlorination of Chlorinated Solvents
Rebecca Jackman, MIT	Liquid Phase and Multi Phase Microreactors for Chemical Synthesis
Aleks Franz, MIT	High Temperature Gas Phase Catalytic and Membrane Reactors
Patrick L. Mills DuPont Central Research & Development	Microfabricated Gas-Phase Reactor: Scale-Up & Packaging
Louis C. Chow University of Central Florida	Mesoscale Refrigerator
Haim Bau University of Pennsylvania	Microfluidic Components and Systems Fabricated in Low Temperature Co-fired Ceramics Tapes
Anantha Krishnan	Computational Design Tools for Micro-Chemical Systems

4. Summaryof Oral Presentations

Provided by Dr. Patrick L. Mills, DuPont, Research and Development, Experimental Station

4.1 Conference start

Professor Klavs Jensen gave the welcome address from MIT with other remarks given by Peter Fedkiw from NC State University/Army Research Office (ARO). The meeting was sponsored by the ARO and the Defense Advanced Research Project Agency (DARPA). The other members of the organizing committee were Robert Nowak (DARPA) and Dick Paur (ARO). Robert Nowak mentioned that one big program is in development of fuel cells as replacements for batteries that are typically carried by the foot soldier in the Army. Another obvious problem is the use of hydrogen in current fuel cell technology. He showed a schematic of a microcombustor/heat exchanger that would take a logistics fuel and convert it to hydrogen or clean fuel. He also mentioned the meso-machines program that is being sponsored by DARPA.

Professor Jensen next reviewed the workshop objectives, which include a review of the state-of-the-art in microchemical systems for chemical and analysis systems. He also summarized

typical applications in MEMS (Micro Electro Mechanical Systems), with rapid growth is being experienced in biology and pharmaceuticals. He also mentioned the Laboratory on a Chip work of Burns et al. (*Science,* **282**, 404 (1998)) and Jed Harrison from Alberta. The motivation for using microchemical systems was also described along with various energy generation devices developed at PNNL.

4.2 Plenary Session: Microchemical Systems and Applications

4.2.1. "Microreactor Components and Systems -Basic Properties, Fabrication Methods and Commercial Applications,"

Wolfgang Ehrfeld, IMM, Mainz, Germany

This talk covered applications, commercialization and recent developments in microreactors. Their fundamental properties include their physical size and number of units. The applications are in process development and in production, which allows distributed production and reduces safety hazards. A recent application includes liquid-liquid and gas-liquid mixing where small droplets can be generated. The size is controlled by flow rate ratios (*see I&EC Res.*, 1075 (1999)). The development of a heat exchanger with counter-current flow (see Ullman's Encyclopedia, Microreactors, 1999). The R&D of a liquid reactor showing the step-up response was also illustrated.

A review of microfabrication processes was given next, that included more than 10 steps. The use of lithography to develop 3-D structures was shown based on the LIGA technique. The use of layered structures was shown, which are commercially available. The design of a 96-channel electrophoresis chip was described. Recent microreactor developments were reviewed next. The design of micromixing devices made from a wide range of technologies was also shown. An example of an annular mixture device was described, including a flow simulation of a high throughput mixer. Applications in cosmetics, pharmacy, and other areas were mentioned. The final discussion was on modular systems for lab automation and an example of their use in multiphase reactors. Examples of falling film reactors, micro bubble columns, and other systems along with the synthesis of propenoxide and anisaldehyde were mentioned. Final comments were on scale-up of chemical reactors.

4.2.2. "Integrated Reaction, Separation, and Detection Systems for Biochemical Analysis,"

Professor Mark Burns, University of Michigan, Department of Chemical Engineering

Professor Burns compared the traditional versus integrated systems approach to DNA synthesis. The motivation for this work is for the human genome project, which requires new developments before it can be achieved. Miniaturization and integration techniques were reviewed and discussed. The requirements for making integrated devices were described, which included compatibility and simplicity. A discussion of microfluidics and key aspects of reaction systems was given, along with separation systems. An integrated DNA analyzer was illustrated, which combined sample loading, drop metering, thermal reaction, gel loading, and analyte

detection. It uses 100 nl drops with control within ±0.1°C. Construction is based on photolithography, which was supported by a number of photographs. The remaining discussion was on development of the integrated device, which included reagent metering by modulated input of gas into a flowing liquid stream with hydrophobic/hydrophillic sections to control wettability. To create pressure, a small chamber containing gas was heated as a means of splitting liquid into droplets. The use of temperature and surface tension to create drop movement was described. Key aspects of temperature control and ability to control and monitor this variable were summarized. The methods for separation and detection of the DNA were quite interesting, which included the use of fluorescence. Typical data obtained from tuberculosis DNA, which involve integration of the above operations, was shown as a demonstration of the technology. The final part reviewed the various types of materials that were being investigated for the various operations.

4.2.3. "Recent Results of Chemical Syntheses on a Microfluidic Chip,"

Rolf Swenson, Orchid Technologies

This presentation was concerned with the use of massive parallel arrays for acceleration of drug discovery. The motivation included decreased cost, higher throughput, increased analytical sensitivities, and seamless integration. Detection is performed by LC/MS for precise identification. The platform technology uses parallel processes via multilayer structures and precision microfluidics so they can deliver nanoliter quantities. Fluid delivery is done by a capillary break mechanism. This is more repeatable than a serial type system for dispensing. Use of a vacuum to clean the dispensing well was shown. Heating and cooling between 25°C to 100°C was also described. The wells were 1.5 mm x 1.5 mm x 0.3 mm with a volume of 650 nl with 200 μm particles. A 3-D sketch of a microfluidics chip showing the plate and layer design for control of venting, pressurizing, filling, and other operations was given.

Orchid's current chips contain either 96 wells, 384 wells, or 1536 wells. To automate the liquid titration, a conventional robotic system was used. The demonstrated reactions include solid phase and solution phase chemistries. The limitations include using systems with solids, operation at high pressure, and use of corrosive fluids. A method for testing for contamination and assessing the quality of titration and other operations showed that it was quite reliable. They have also studied performing LC/MS analysis on the order of seconds versus minutes. An analytical collaboration has been developed with Advanced Bioanalytical Systems in Ithaca, NY. The electrospray is created at 100 nl/min of flow through a 20 μm hole in a chip.

4.2.4. "Gas Phase Chemical Detection with an Integrated Chemical Analysis System,"

Steve Casalnuovo, Sandia National Labs

The idea here was to summarize methods for performing gas phase chemical analysis in a portable unit. It is battery powered and can be used for both gases and liquids. The box has a characteristic dimension of 9 inches. The driver for this unit originates from national security issues, e.g., mine detection, counter-terrorism, etc., although other applications were envisioned.

A schematic design of the system was shown, which included the typical elements of a GC. The system contains a concentrator that increases the sample concentration and is a miniature hot plate based on a Si_3N_4 membrane. The heating rate is rapid, e.g., 20 → 200°C in 10 ms using 45 mW over a 2.2 mm^2 plate. The pulse widths are about 200 ms. Tailored sol-gel materials are used for high uptake and selectivity. They are tailored for each application, e.g., detection of nerve gas, solvents, and other chemicals.

The GC column is based on etching deep spiral channels into silicon in which the stationary phase is coated into the thermally oxidized wells. The channels are 80 μm wide by 240 μm deep. A chromatogram on a 40 μm x 250 μm x 1 m column at 40°C was shown with elution times between 10 to 20 seconds. Detection is accomplished using an array of surface acoustic wave (SAW) chemical sensors that operate between 100 MHz to 1 GHz. The device is fabricated on a quartz substrate with wiring traces produced using photolithography. It was shown that the SAW array responds differently to particular compounds. Aspects that were not discussed included packaging, liquid-phase chemical detection, and pattern recognition algorithm for data analysis. Future efforts will focus on temperature programming the column and development of higher frequency GaAs surface acoustic wave sensors. It was speculated that the preloaded concentrators may serve as a thermally activated reagent source, and the concentrator cavity may serve as a reaction chamber with thermal sensor as a membrane.

4.3 Plenary Session – Chemical and Fuel Processing

4.3.1. "Microchemical System Applications - DuPont Experience,"

James F. Ryley, DuPont Central R&D

Dr. Ryley gave an overview of research performed at DuPont in minichemical systems over the past 10 years. The initial section summarized the drivers for using microreactors and the collaborations that occurred between DuPont and MIT. Candidate reactions in the early work were mainly concerned with manufacture of hazardous chemicals at small (< 1 x 10^6 lbs/yr) production rates. The gas phase reaction of butyl isocyanate was one of the first applications conducted in a laminated structure with mixing, heat exchange, reaction, etc. This was followed by methyl isocyanate by oxidation of methyl formamide over silver at T = 500 – 650°C, which is normally practiced in two stages. A staged microreactor design was developed that incorporated staged oxygen injection and heat exchange. The use of microreactors for manufacture of HCN and TFE was also mentioned, particularly the Andrussow and Degussa processes. The use of ceramics in lieu of silicon, since silicon can form metal silicydes, was mentioned.

Another interesting example was the solventless spinning of Lycra®, which has issues of liquid-liquid mixing, high-pressure operation, and fast reactions. The design of a spinnerette head for *in situ* reaction and fiber spinning was illustrated. All of the above work was performed up to ca. 1994.

The next section reviewed the MIT-DuPont program as part of the DARPA Microflumes program effort. The tasks included reactor development, modeling, process control and packaging. An overview of the detailed micro reactor modeling, selected applications, e.g.,

ammonia oxidation and methane oxidation, and key aspects of packaging using a TI DieMate® socket was given. The final part described key aspects of the process control and instrumentation for this project, included cold-flow testing and use of LabView® as the data acquisition and control system.

4.3.2. "Hydrocarbon Fuel Processors - Development Issues in Fuel Cell Vehicle Applications,"

Richard Bellows, Exxon Research & Engineering

This presentation first gave an overview of proton exchange membrane (PEM) fuel cells that use hydrogen to produce power. Various fuel options were summarized that included the technology requirements, economics, environmental impact, infrastructure, and distribution. Key aspects of vehicle hydrogen production via fuel reforming were summarized. These included use of hydrocarbons or alcohols as chemical H_2 carriers (e.g., $C_8H_{18} + 4\ O_2 + 8\ H_2O = 17\ H_2 + 8\ CO_2$ and $CH_3OH + H_2O = 3\ H_2 + CO_2$ (steam reforming or SR). The advantages of liquid fuels and challenges were summarized.

Most work at Exxon has been on the conversion of gasoline. The key chemistry used POX/SR followed by water-gas shift.

POX: $C_8H_{18} + 4\ O_2 = 8\ CO + 9\ H_2$ (+ heat)

SR: $C_8H_{18} + 8\ H_2O$ + heat $= 8\ CO + 17\ H_2$

WGS: $CO + H_2O = CO_2 + H_2$ + heat

Key concerns include effect of impurities that cause problems for the reformer, soot formation at high temperatures, and heat integration. The fuel train strategy was reviewed for each of the above steps with a focus in advantages and disadvantages.

Equilibrium calculations were used to illustrate soot formation. The basis used was H/C = 1.8, O/C = 1.05, and p = 3 atm. Species shown were CO_2, H_2O, CH_4, CO, H_2 and C(s) over 100-1200°C. Carbon deposition limits were illustrated vs. water addition using O/C = 0.75 $\rightarrow$ 1.1 and H_2O/C from 0 $\rightarrow$ 1.4. It was shown that carbon deposition depends on the C/H/O ratios and temperature by using a ternary diagram.

Discussion on the water-gas shift reaction suggested that key issues include the volume/weight of the catalyst and time required to achieve startup. More active catalysts are required. The PROX selectivity was shown to decrease at high conversion (see *J. Catalysis*, **170** (1), 1997). A CO concentration of less than 5 ppm is needed. The overall system efficiency for an iso-octane POX reformer train was evaluated for an ideal vs. practical case. The ideal system had an overall efficiency of 47%, while the practical one had an overall efficiency of 35.8%. The assumptions used for the latter were η_{CH4} = 96% (POX), η_{CO} = 97.3% (WGS), η_{PROX} = 97.3% (PROX), η_{bleed} = 97.7% (O_2 bleed), and $\eta_{H2\ util.}$ = 85% (PEFC).

Part II of the talk reviewed hydrocarbon processor development issues. Issues on logistic fuels included the higher boiling range of diesel fuels (150 – 370 vs. 40 – 200°C), lower H/C ratios (1.6 vs. 1.8), effect of higher sulfur levels (500 – 2000 vs. 0 – 50 ppm), and impact of aqueous impurities, such as NaCl, carbonates, and sulfates. In conclusion, a hydrocarbon

processor must compete with existing technologies from the perspective of operability, life and cost. Also, logistic fuels are more difficult to process versus gasoline.

4.3.3. "Fuel Processing in Microchannel Reactors,"

Anna-Lee Tonkovich, Pacific Northwest National Laboratory

Funding for this work is from DARPA and the DOE-EE Office of Transportation Technology. Key players include Bob Wegeng and Michelle Friedlich. The opening slides summarized the key sizes of microsystem components and comparisons between conventional process hardware. The focus here was on fuel processors for automotive power. The drivers for the latter include efficiency (50% vs. 20% for an IC engine), size, cost, and environmental (58% reduction in CO_2). he issues in development of a portable power source were described. Diesel has the greatest energy potential followed by hydrogen storage using metal hydrides. Patents that teach laminate sheet were quickly summarized, which were issued in 1997 and 1998.

The block diagram for a fuel processor system was shown. Key components included a vaporizer and water-gas shift reactor, power generator, and CO clean-up system. Each component was reviewed in detail. The pros and cons of partial oxidation, autothermal reforming, and steam reforming were listed. The latter was touted as the preferred approach over the others. The key reactions are

$$C_8H_{18} + 8\,H_2O = 8\,CO + 17\,H_2 \text{ (1345 kJ/mole)}$$

$$CO + H_2O = CO_2 + H_2 \text{ (some high T shift).}$$

A proprietary catalyst was claimed to give > 90% conversion and > 90% selectivity to hydrogen at 650°C and 3-10 ms of contact time. This was incorporated into a 1 cu.in. reactor with a vaporizer and other components. Some time-on-stream data showed up to 40 hours of running operation with negligible deactivation.

Data on the water-gas shift reactor at 300°C, a H_2O:CO of 3:1, with 5% CO in the feed were shown. Equilibrium conversion was ca. 99%. A detailed design for a gasoline vaporizer was also shown. Its size was 3 in. x 4 in. x 5 in. It could handle 1400 SLPM with a $\Delta P < 2$ psi. The design of a portable power system with 10 W-hr output was shown whose size was on the order of a coin.

4.3.4. "Catalytic Partial Oxidation at Millisecond Times,"

Lanny D. Schmidt, University of Minnesota

Professor Schmidt views 10,000 microreactors in parallel as a system that is analogous to a monolith. Applications covered include methane to syngas, ethane to ethylene, and other hydrocarbons to oxygenates. Porous foam, monoliths, or gauzes containing Pt, Pd, and Rh are used as catalysts. Materials include α-Al_2O_3 foam, etched nickel, fibermat, and related materials. The reactors typically operate at 900-1200°C using a contact time of less than 5 ms in a fuel-rich mode.

In methane oxidation, the potential reactions are

$$CH_4 + \tfrac{1}{2}\, O_2 \rightarrow CO + 2\, H_2 \quad \text{(desired)} \tag{1}$$

$$+ 2\, O_2 \rightarrow CO_2 + 2\, H_2O \quad \text{(undesired)} \tag{2}$$

$$\rightarrow C(s) + 2\, H_2 \quad \text{(undesired)} \tag{3}$$

or

$$CH_4 + H_2O \rightarrow CO + 3\, H_2 \tag{4}$$

Results were shown using 45 ppi Rh monolith catalyst, $CH_4/O_2 = 2.0$, $T_o = 25°C$, and T = 5 ms (from Dietz, 1995) at pressures between 1 to 30 atm. He showed that a linear scaling assumption would produce 500 tons/day for a 1.5 foot diameter unit.

For ethane oxidation, the key reactions include

$$C_2H_6 + O_2 \rightarrow 2\, CO + 3\, H_2 \text{ (undesired)}$$

$$C_2H_6 + \tfrac{1}{2}\, O_2 \rightarrow C_2H_4 + H_2O \text{ (desired)}$$

plus other reactions. Data was given using Pt/Al_2O_3, and showed 65% C2H4 selectivity and 60% C_2H_6 conversion, which is less than a conventional thermal processes. By adding H_2, selectivity was improved to ca. 85-90% at a H_2/O_2 of 3:1. The role of homogeneous and heterogeneous oxidation was compared using detailed computer simulations to assess the impact of pyrolysis chemistry.

Discussion next shifted to cyclohexane oxidation using 90% Pt – 10% Rh on a 40 mesh gauze. The dominate olefin is cyclohexene, while the dominant oxygenate is 1-hexen-al. The design and use of a heat exchange reactor where catalyst is deposited so endothermic and exothermic reactions can be operated efficiently was also described.

4.3.5. "Combustors for Micro Heat Engines,"

Ian A. Waitz, Department of Aeronautics, MIT

Professor Waitz gave an overview of the MIT microengine project. Applications occur in various power generation devices, such as turbines. The idea is to shrink a macro turbine down to a tiny version having a power output of ca. 50 watts and a small number of mechanical components. Applications are in portable power systems and micro air vehicles where the latter have an overall length on the order of 10 to 12 cm. The physical requirements include high peak cycle temperatures (1200 – 1700 K), high peripheral speeds (400 – 600 m/s), low friction bearings, and reasonable component efficiencies.

An overview of the micro-engine fabrication process was explained using a cross-sectional view of the device. The combustion chamber uses the greatest volume, while the journal bearing is the most critical component. Micro bearings have been operated to 500,000+ RPM. Heat transfer effects are the most severe transport limitation. Power density calculations show that a heating rate for a micro system is ca. 3×10^5 MW/m^3-atm which ca. ¼ of commercial systems. Residence times in the burner are about 1×10^{-5} ms. These put severe limits on materials and heat transfer requirements.

The hydrocarbon flammability limits translate into use of a two-zone process for many applications. Other key factors are that viscous effects are more important, some materials are stronger than others, and effective diagnostics for troubleshooting do not exist when compared to large combusters. Simulation of the transport using existing CFD codes is also quite difficult. The final discussion summarized key challenges in modeling and development of the hydrocarbon combustion zone. Power density and pressure drop become limiting. Key issues and needs include high temperature materials fabrication, diagnostic devices that can be used with micro devices, fuel delivery/throttling/vaporization systems, thermal management, and catalytic/ hydrocarbon modeling and simulation. The importance of multi-disciplinary teamwork was also mentioned as being critical to program success.

4.3.6. "Manportable Microtechnology Based Absorption Heat Pump,"

Michele Friedrich, Pacific Northwest Batelle Laboratory

Research was described on the development was described on single-effect absorption heat pumps using micro-technology with heat flux of 100 W/cm^2 that are hand-held. The absorber film thickness was on the order of 50-150 μm. The evaporator has an overall heat transfer coefficient U = 3600 – 7400 W/m^2-K (200-420% of conventional), while the absorber U's are similar in their characteristics. Applications are in man-portable climate control suits, vehicles, food storage, and other related systems.

A prototype man-portable single-effect LiBr unit has been developed that can produce 350 W of cooling using rechargeable batteries for powering the fans. It has a weight of 5.1 kg and can operate for 10 to 12 hours.

4.4 Plenary Session - Materials and Microfabrication

4.4.1. "Microfabrication and Microfluidics Using Polymers and Rapid Prototyping,"

George M. Whitesides, Harvard University

The idea behind this approach is to create a CAD file of the prototype mask that is printed using a 3300 dpi laser image print, which can resolve 20 μm lines. This is then used to create a photolithographic mask. Replica molding is also possible using polymer molds. The edge resolution is about 100 nm roughness. By using a microfiche photo mask, rapid prototyping is also possible. These techniques have been used in capillary electrophonesis with a microscope as a detector.

Example applications in microwave guides and microfluidic diffraction gratings were illustrated. Fabrication of microfluidic channels around capillaries to form a helix was illustrated with a characteristic dimension of 2 mm. Another application was the development of a microfluidic pump. Another approach for making a carbon fiber structure was to first make a polymer mold of carbon-filled fibers. It was then burned out which left the desired structure behind.

The discussion next turned to fabrication of microfluidic channels with knots to form 3-D structures. A method for selectively filling wells in an array based on discontinuous wetting was described. He showed how to fill the holes selectively, and also how to use laminar flow in a capillary to fabricate electrochemical detectors .

4.4.2. "Novel MEMS fabrication approaches,"

Martin A. Schmidt, Dept. of Electrical Engineering, MIT

Professor Marty Schmidt from MIT spoke on the benefits and disadvantages of silicon micromachining. Opening comments were aimed at pointing out difficulties with using silicon, such as access to the technology, manufacturing favors high wafer volumes, it is fundamentally open-loop manufacturing, the IC industry protocols are cumbersome, and costs are high. Despite these, silicon has benefits due to its properties, existing knowledge about it is abundant, and owing to its high reliability.

He next gave an overview of the deep reactive ion etch process (DRIE) and related material properties. Etching parameters are many, including SF_6 flow rate, electrode power, active cycle duration cycle overlap and cycle power. Similar variables affect the passivating cycle using C_4F_8. Application of the technology in etching 1 □m wide trenches for the micro-turbine program were outlined.

Professor Schmidt also described a device for aligned wafer bonding. He then described applications in liquid-phase microreactors, micromolding, and the micro-turbine project. In the MIT engine program, a turbine rotor having a 4 mm diameter was fabricated and tested using a special purpose microbearing rig. To release the rotor after fabrication, an 8W argon ion laser is used as a part trimmer. He mentioned that key technology lessons learned are associated with DRIE plus wafer bonding and DRIE manufacturing techniques.

4.4.3. Microfluidic Systems Fabricated in Low Temperature Co-fired Ceramic Tapes

Haim H. Bau, University of Pennsylvania

This presentation described the use of ceramic tapes to create mesocopic. Devices are made by machining each layer to form the desired patterns. In the green state, ceramic tapes are soft, pliable, and easily machinable. The material facilitates easy fabrication of mesoscopic features. In the fired state, small and precise structures can be machined using diamond tools, abrasive jets, and/or lasers. It is possible to cast tapes of various ceramic compositions to obtain desirable properties. Thus, desired properties such as low/high thermal conductivity, and piezoelectric and magnetic layers can be obtained. Large number of layers can be laminated to form three-dimensional structures. A well developed thick film technology facilitates the deposition of various metals and electrical components on the tapes in the pre-fired state and the formation of three-dimensional interconnects. It is possible to fabricate hybrid structures consisting of ceramics, silicon, metals and/or some other suitable materials. Professor Baum described the fabrication process, potential problems and their solution. He also gave a number of examples of applications, including hydraulic interconnects, a flow meter, a thermal cycler and PCR reactor, an electrophoretic cell, an impactor for inertial separation of particles, and a fluid mixer.

4.5 Banquet Presentation - "Mesoscopic Machines - There is plenty of room in the middle!"

Lawrence H. Dubois, DARPA/DSO

Dr. Dubois, the Director of DARPA Defense Science Office, gave the workshop banquet presentation. He spoke about the opportunities for mesocopic machines - sugar cube to fist size. These devices bridge the size range between conventional machines and MEMS. They provide for enhanced heat, mass and momentum transport and represent an optimal size range for a wide variety of chemical reactions and fluidic functions. Larger systems are difficult to accurately control, in particular surface chemistry, heat and fluid flows. Thermal and fluidic properties in smaller devices are dominated by wall interactions and these devices tend to have high pressure drop and low throughput. Mesoscopic machines operating in parallel may replace large systems with resulting improved reliability and reduced manufacturing costs. Technical issues in realizing mesoscopic machines were delineated, specifically device design/ scaling laws for fluids, chemistry, combustion, etc.; fabrication of three- dimensional shapes and structures; materials and materials properties, and systems *vs.* components. Dr. Dubois described a number of application examples of small machine for which the mesoscopic size range was optimal. The examples included bistable electrostatically activated mesoscopic pumping, electrostatic meso-cooler for person cooling, water purification systems, and mesoscale turbine engines. The talk also provided an overview of several three dimensional prototyping fabrication techniques for mesoscale systems.

5. Working Group Reports

5.1 Working group 1: Opportunities for MicroEnergy Devices

Robert Wegeng - PNNL (Leader)

Summary by Aleksander Franz, MIT

The group determined several exciting areas for potential application of microreaction technology and key scientific issues associated with development of this technology. The group participants identified the essential features of microchemical systems, which make them potentially highly relevant in small power generation devices. A list of applications where microreaction technology could have the highest impact was generated. Several scientific and engineering problems in realizing the microreaction technology were identified. These problems were used to generate areas of research and development which could enable future implementation of microchemical systems in microenergy devices.

The small dimensions of microchemical devices result in uniquely high surface to volume ratios, compared to traditional chemical processing equipment. The high surface to volume ratios are associated with excellent heat and mass transport properties within the microchemical devices. The high mass transport rates enable fast catalytic reactions, while high heat transfer rates enable high energy density reactors and heat exchangers. Since chemical fuels possess energy densities two orders of magnitude higher than rechargeable batteries, application of microchemical devices in fuel processing for power generation could result in much higher energy densities than batteries.

The power generation applications envisioned for microchemical systems are those which can most benefit from the assumed improvement in energy density. Some examples include soldier power, remote/off-grid power generation, stationary rechargers, camping, robotics, guided munitions, distributed sensing systems, and backup power. The group focussed on two applications with highest impact potential: soldier power and soldier cooling. While the high weight and low energy density of batteries puts severe restraints on soldier performance, soldier cooling is currently not practical with available technologies.

Two power generation approaches were considered in microchemical systems. One was a fuel reformer combined with a fuel cell. The other was combustion, combined with thermoelectric elements, thermophotovoltaics, or alternative thermal cycles. Although other, more desirable power generation schemes may be developed, the scientific and engineering challenges in this group were envisioned primarily in the context of the above technologies.

Development of microchemical power generation systems represents a departure from traditional engineering approaches. The small scale of the devices dramatically changes the heat and mass transport properties, increases the importance of surface forces, and generates a novel set of engineering problems which do not apply for conventional scale equipment. Fast heat transport can be advantageous, but it can also be highly undesirable from the standpoint of heat losses. Since similar operating temperatures must be achieved in these small systems with lower throughputs as with conventional systems, and since overall device dimensions must remain

small, device design for heat isolation becomes paramount. Novel materials such as aerogels may have to be utilized as insulators, and novel reactor design geometries may be necessary. Small channel dimensions can be more susceptible to fouling and plugging. Small system dimensions also make packaging and interfacing to the often macroscopic surroundings challenging. Micro/meso fabrication methods may eventually produce ultra compact equipment usually thought of as peripheral, such as pumps, valves, fans, filters, etc. However, the overall system performance (efficiency, reliability) will depend much more directly on these micro-peripherals than in large chemical processing systems. High processing temperatures also dictate the use of high temperature materials, and appropriate fabrication methods must be devised to integrate these materials. Device fabrication is also challenging, and truly three-dimensional microfabrication approaches are scarce. Lack of fabrication capabilities often forces a compromise between the optimal design and one that can be fabricated. The choice of fuels is also an important engineering consideration. The fuel dictates the processing needs, and although logistics fuels are desirable, the simple, single chemical fuels offer advantages in terms of processing demands, purity, and fouling that could make the difference for technology feasibility. Finally, short chemical residence times in microchemical devices require highly optimized catalysts and adsorbents and methods for effectively integrating these materials into the overall fabrication process.

In light of the above demanding problems, a number of critical, cross-cutting research areas were identified. Novel thermal insulating materials and thermal device designs must be pursued for the microchemical energy systems. Micro and meso fabrication approaches need to be extended to enable more flexible device design and integration of catalysts, adsorbents, insulators, and high temperature materials. Peripheral microchemical equipment such as pumps and valves needs to be developed specifically with the goals of small power generating systems in mind. Such peripheral equipment would be small, light, and utilize minimum power. Platforms for effective and flexible overall system integration of various unit operations, batteries, controllers, fuel tanks and environmental interfaces must be designed and implemented. Basic experimental and modeling research should continue to improve understanding of reacting, non-reacting, single phase, and two phase flows in small channels. Finally, microchemical reactors and heat exchanger designs must be fabricated and quantitatively assessed to enable systems level projections of power generation efficiency. Because the physics associated with scaling down microchemical systems often do not conform to conventional scale engineering wisdom, a new set of engineering rules and intuition must be developed to reflect the experience of designing, fabricating, and quantitatively testing microchemical devices.

5.2 Working Group 2: Challenges and Needs in Microfabrication and Materials

Martin A. Schmidt - MIT (Discussion Leader)

Summary by Rebecca Jackman and Martin Schmidt (MIT)

The requirements for specific applications drive the need to extend existing techniques for microfabrication and to produce microstructures in materials other than silicon. Applications in

the area of microchemical systems that the working group considered were devices for chemical synthesis, systems for power generation, total microanalysis systems, and devices for environmental remediation. (BioMEMS were discussed briefly but were agreed to lie beyond the mandate of this workshop.) Challenges in fabricating these types of microchemical systems arise because of various practical constraints: the devices may need to withstand extremes in temperature, high pressures, and harsh chemical conditions. These requirements must be met while components that perform multiple functions are integrated, precision in fabrication is maintained, and an appropriate packaging solution is developed. All of these needs must be met within a reasonable period of time and at a tolerable cost.

Once the specific needs for an application have been identified, the optimal material(s) for fabrication can be selected. The choice of material then determines the methods available to the designer for fabricating the device. We identified five basic classes of materials that are of interest to an engineer designing a microchemical system – we discussed techniques for processing these classes of materials (the state-of-the-art), and the advantages and limitations associated with each of them. Recommendations for improving fabrication methods for these materials were identified. The table that follows summarizes these discussions.

Two issues in the discussion of the fabrication of microchemical devices were recurrent: how to design systems that incorporate different materials and how to package these devices. If it is going to be possible to incorporate different materials into microchemical devices, then it is essential that methods for integrating and bonding dissimilar materials be developed. Currently, lamination of patterned sheets is the dominant method for bonding complex microstructures. While there is no general solution to the bonding problem, it is an area that we identified as critical for improvements in the fabrication of these, and other, miniaturized devices. The other issue that is relevant to all systems is the question of packaging: should fabrication be integrated or modular? The consensus was that a modular approach would be more flexible.

We make several recommendations for the development of an infrastructure that would facilitate the accessibility of the technology for producing microfluidic/microchemical systems. We recommend the establishment of a foundry (perhaps virtual) that would serve as the starting point for this infrastructure (cf. MCNC Foundry for MEMS community). The foundry would provide micropatterned sheets of ceramic, silicon, metal, etc. and would develop methods for bonding these sheets to an integrated device. Standardization of both fluidic and electrical interfaces within the foundry, and the creation of design rules for devices, would streamline processing and would ultimately facilitate the development of standardized packaging solutions. Within the foundry a database of materials properties would be established, and the processes would be modeled for process engineering.

Material	Fabrication Methods	Advantages	Limitations	Recommendations
Ceramics	Laser machining, Powder processing, Solid-freeform machining, Sol-gel processing, Chemical vapor deposition, Micromolding	Resistant to chemically corrosive environments and high temperatures	Dimensional stability (warpage and shrinkage, precision) Porosity Brittleness Problems with integration	Develop methods for fabrication at the micron scale
Plastics	Injection molding, Embossing, Micromolding, Solid-Freeform Machining	Cheap (low cost at high volume throughput) Easily prototyped Good optical properties Biocompatible	Incompatible with many classes of chemicals (depends on specific polymer) Large coefficients of thermal expansion and poor stability at high T Limited strength and durability	Improve access to rapid prototyping
Metals	Milling, Laser processing, Electroforming/electroplating Electrochemical/electrodischarge machining (ECM/EDM), LIGA	Large material properties knowledge base Cheap Widely accessible Good thermal and electrical properties	Limited precision in conventional machining	Develop methods for high precision micromachining of bulk metals
Semiconductors	Wafer processing (IC)	High strength No creep High temperature capability (~600°C) Good electronic properties Large material and process knowledge base Easy to machine with high precision Large and reliable support infrastructure	Limited access to facilities (capital intensive) Manufacturing favors high wafer volumes (~10,000 wafers/mth) Fundamentally open loop manufacturing (run-by-run control) Cumbersome IC industry protocols (slow cycle times) Cost of material and process	Develop methods for integrating Si with other materials
Glass	Dry etching, Wet, isotropic etching	Good optical properties Reasonable temperature stability Biocompatible	Limited methods for micromachining	Develop alternative methods for micromachining, e.g., robust methods for etching

5.3 Working Group 3: Chemical Applications of Microchemical Systems

Klavs F. Jensen - MIT (Discussion Leader)

This working group assessed chemical applications of microreaction technology; specific opportunities were discussed along with research needs and barriers to implementation. Energy and fuel processing applications were excluded since Working Group 1 covered them. In order to focus the discussion, the working group defined microchemical systems as having the following characteristics:

(i) chemical transformations take place,
(ii) a precisely controlled design,
(iii) fabricated by microfabrication techniques including MEMS methods, soft lithography, and micromachining,
(iv) fluidic channel dimensions range from sub millimeters to sub micron, and
(v) scale-up of production by replication ("numbering up" or "scale-out").

The integration of sensors (flow, pressure, temperature and chemical species) and actuators (heaters and valves) with reaction channels was desirable but not necessary for a device to be a microchemical system. The group chose to focus on microchemical systems for synthesis. Devices combining reaction, separation, and sensing with the primary aim of chemical or biological diagnostics ["laboratory on a chip" or micro total analysis systems (μTAS)] were considered outside the scope of the workshop.

The workshop presentations and posters had shown existing applications of microreaction technology, including DNA analysis, combinatorial chemistry, partial oxidation of hydrocarbons, isocyanate synthesis (DuPont), vitamin intermediates (IMM-BASF), fine chemicals (IMM-Merck - Germany), and specialty polymers (IMM-Aventis). The group identified a number of additional applications for different chemical industry segments, which are discussed below. Table 1 lists a number of specific examples the group projected would be realized three and ten years out.

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- *Devices for medical diagnostics* - This field is rapidly expanded with a number of large companies (e.g., Motorola, Agilent (HP), and Perkin Elmer) and small companies (e.g., Caliper and Aclara) driving development. This application is closely related to μTAS and beyond the scope of the workshop.

- *Personal care and cosmetic products* - The controlled micromixing achievable in microchemical systems has potential for producing emulsions and creams with substantially reduced amounts of surfactants and other additives that might interfere with the intended

application. Products with a short shelf life that could be produced by mixing and reaction in a small device (perhaps integrated with the chemical reservoirs) are potential targets for microreaction technology. The potential for chip-based, time-controlled drug delivery was recently demonstrated[4] and the concept can readily be extended to other microreactor configurations.

- *Fuels and energy* - In addition to the specific applications of fuel processing for hydrogen generation for PEM fuel cells and thermal energy conversion, discussed by Working Group 1, microreactors could be used for specialized fuel upgrading and processing applications with high cost low volume characteristics.

- *Laboratory and pilot plant instrumentation* - Microreactors integrated with sensors and actuators would provide efficient platforms for generation of transport and kinetic data needed for process scale up. Scaling from the laboratory to the pilot plant could be done by numbering up microreactors. Microreactors are natural platforms combinatorial approaches, as well as statistically planned experimentation.

- *Biochemical processing* - Microreactors with enzymes have been demonstrated for μTAS applications, and existing hollow fiber reactors could be considered as microreactors in the sense that the fiber thickness falls in the sub millimeter range. Additional potential application areas include microfermentation systems for screening and directed evolution, as well as fed-batch reaction systems with controlled environment for cell free protein synthesis.

- *Pharmaceutical and fine chemical production* - Typical reactions such as halogenation, nitration, oxidation, and hydrogen offer opportunities for microreactor technology. The improved heat and mass transfer could lead to higher conversion and selectivity while also yielding a safer and cleaner production. Moreover, the flexibility of numbering up units in scale up would allow capital investment and production to be aligned with product demand. This approach would lower the risk and cost of introducing new products while also accelerating the transfer from laboratory to pilot plant and production.

- *Sustainable development - environmental friendly production* - Adopting microchemical systems would change production from traditional batch reactors to small continuous processes with lower process inventory, and thus, less possibility for potentially damaging spills. The excellent heat transfer characteristics in microsystems would reduce or eliminate the need for use of solvents for dilution to avoid thermal runaway reactions. Moreover, microchemical systems would enable more efficient contacting schemes and new reaction sequences with fewer process steps and improved yields. By integration of microreaction elements with separation units it may be possible to further improve yields and minimize waste. The use of microreaction technology would also have the potential for on-site, on-

[4] Santini J, T., Cima M.J. and L. R., "A Controlled-Release Microchip," *Nature*, **397**, 335 (1999).

demand production of highly reactive and toxic intermediates, reducing or eliminating the storage and shipment of such compounds.

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Difficulties in applying microreactors will arise when dealing with "sticky solids" and "dirty" systems, leading to fouling of the reactor channel. Microreactors are also less likely to be successful when high surface area to volume is a problem for the process. Surface adsorption, contamination, and unintended catalysis could be side effects of the high surface to volume ratios characteristic of microreactors. The low throughput per unit is perhaps the most serious shortcoming of microreaction technology. For this reason microreaction technology should not be viewed as a means for miniaturization of existing processes, but rather as a tool for realizing new processes under more aggressive, better contacting conditions where reaction rates and product yields are higher than in standard reaction equipment.

Table 1. Examples of microreaction applications three and ten years out.

3 years	10 Years
Combined chemical synthesis and analysis Decontamination chemistry Fogs and emulsions Portable fuel processing Potable water and air purification Personal medical devices BioChem detection Increased use in discovery and pilot plant Exponential growth in production of fine chemicals	Exponentially decreasing cost of chemical information 10^3 types of microTAS 30% of fine chemicals produced by microchemical systems Personal chemistry devices Microsystems available for particular reactions/chemistries Microsystems for materials synthesis Small to medium size industrial base for microchemical systems

[5] Santini J, T., Cima M.J. and L. R., "A Controlled-Release Microchip," *Nature*, **397**, 335 (1999).

Advances in microreaction technology will require multidisciplinary research approaches. Research must be done in relevant areas of transport phenomena, chemistry, materials, and fabrication technology to realize the promise of microreaction technology. A better understanding of mixing and flow in microchannels is needed for simple and complex fluids. Simulation tools exist for simple laminar Newtonian flows, but applications will require quantitative predictions of complex flows and novel mixing schemes. Quantitative models of electrical field driving flows (electroosmotic flows) or separations (electrophoresis) must be included in transport simulations. The high surface area to volume characteristics of microreactors drive the understanding of surface chemistry in microchannels. Fundamental insights into adhesion and surface modifications could lead to the development of surface coatings preventing undesired adhesion of molecules from the fluid stream—an important consideration for biological systems. The use of molecular self-assembly methods could be used to develop micro- and nano-structured composites for catalysis. Surface coatings control surface tension and, therefore, also can be useful in manipulating fluid delivery.

Description of microchemical device performance must be based upon a systems approach that integrates chemical, transport, mechanical, and electrical components along with an economic analysis. Models must also reflect the multiple length and time scales involved in microreaction technology. It will also be essential to understand process transients and to integrate process control in the early stages of microreactor design considerations. Answering the question "when is smaller better?" should be central to the development of any microreactor system. Research is also needed on microreactor materials, fabrication methods, and packaging. Working Group #2 discussed these critical issues.

Factors influencing major industrial acceptance of microreaction technology include: (i) demonstrated applications examples; (ii) exposure of the technology to decision makers; (iii) the availability of packaged devices easily integrated into chemical laboratories; (iv) development of fabrication infrastructure (foundries and engineering), and (v) development of standards for integration and fabrication. Research and development of microreaction technology will be enhanced by educational initiatives, specifically interdisciplinary courses, training of process personnel, and development of reviews and texts on all aspects of microchemical reaction technology.

6. Background

Microfabrication techniques and scale-up by replication have fueled spectacular advances in the electronics industry, and they have started to revolutionize biological research and drug discovery. Microfabrication offer a similar potential for faster, cheaper, better chemical product research and development. Micro-chemical systems have feature sizes in the micron to hundreds of micron range, and reaction components are integrated with miniaturized sensors and actuators. The reduction in size and integration of multiple functions create structures with capabilities that exceed those of conventional macroscopic systems and add new functionality.

These developments build, in part, on advances in MicroElectroMechanical Systems

(MEMS)[6]; a field that started by using fabrication techniques developed for microelectronics to construct sensors and actuators but now encompasses a wide range of materials and microfabrication methods. MEMS devices are now found in a wide range of automotive, aircraft, health care, printing, and optical applications. The research investment made in MEMS has enabled the fabrication of microchemical reaction systems. Many of the components (*e.g.*, valves, pumps, flow sensors, mixers, and separation devices) needed in integrated chemical systems have been demonstrated in a wide range of metals, ceramics, and polymers.[7]. Miniaturization of chemical analytic devices in "micro-total-analysis-systems" (μTAS)[8] represents a natural extension of MEMS technology to chemistry and biology with obvious application in combinatorial chemistry, high throughput screening, and portable analytical measurement devices.

Microfabrication offers advantages in reduced consumption of expensive reagents, fluidic components with small dead volumes, improved separation resulting from higher surface to volume ratios, integration of sensors and actuators, parallel screening, and mass fabrication of multiple units by replication. Research laboratories and pilot plant facilities often use small reactors but they are faced with bench top analytical equipment and large panels of complex fluid handling manifolds. With the continual advances in μTAS and microfabricated reactors, these macroscopic test systems could eventually be replaced by PC-card sized microchemical systems consisting of integrated microfluidic, sensor, control, and reaction components. Such systems would clearly require less space, utilities, produce less waste, and offer safety advantages. They would enable high-through-put screening of catalysts and process chemistries under realistic conditions, which has proven difficult in current combinatorial approaches. Moreover, the small dimensions imply laminar flow, making it feasible to fully characterize heat and mass transfer and extract chemical thermodynamic, kinetic, and transport parameters from sensor data.

The reduced consumption of expensive reagents, fast response time, and integration of sensors and actuators inherent in microfabricated systems are particularly attractive for screening of biological samples. Recent DNA detection units are essentially microchemical systems that combine reagent dosing, controlled reaction, separation, and detection.[9] However, microreaction technology will also impact chemical research and production. The high heat and mass transfer rates possible in microfluidic systems allow reactions to be performed under more aggressive conditions with higher yields than achievable with conventional reactors. More importantly, new reaction pathways deemed too difficult in conventional equipment, e.g., direct fluorination of

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[6] K. D. Wise, "Special Issue on Integrated Sensors, Microactuators, and Microsystems (MEMS), *Proceedings of the IEEE* 1998, *86*, 1531-1533.

[7] W. Ehrfeld, V. Hessel and H. Lehr, "Microreactors for chemical synthesis and biotechnology–Current developments and future applications," *Topics in Current Chemistry* ("Microsystem Technology in Chemistry and Life Science") 1998 *194*, 233-252, Springer Berlin.

[8] van den Berg, A. and D. J. Harrison (Eds.), *Micro Total Analysis Systems'98*, Kluwer Academic Publishers, Dordrecht (1998).

[9] Burns, M. A., B. N. Johnson, S. N. Brahmasandra, K. Handique, J. R. Webster, M. Krishnan, T. S. Sammarco, P. M. Man, D. Jones, D. Heldsinger, C. H. Mastrangelo and D. T. Burke, "An Integrated Nanoliter DNA Analysis Device," *Science*, **282**, 484 (1998).

aromatic compounds can be realized.[10] Even if a microreactor failed, the small quantity of chemicals released accidentally could be easily contained. Moreover, the presence of integrated sensor and control units could allow the failed reactor to be isolated and replaced while other parallel units continued to produce. These inherent safety characteristics suggest that production scale systems of multiple microreactors should enable distributed point-of-use chemical synthesis of chemicals with storage and shipping limitations, such as highly reactive and toxic intermediates (e.g., ozone, cyanides, peroxides, azides). As a demonstration of these concepts, DuPont has synthesized a number of potentially hazardous chemicals, including isocyanates, in a microreactor formed by bonding silicon wafers patterned to form channels, preheaters, and catalytic reactor sections.[11]

Scale-up to production by replication of microreactor units used in the laboratory would eliminate costly redesign and pilot plant experiments, thereby shortening the development time from laboratory to commercial production. This approach may be a particular advantage for the fine chemical and pharmaceutical industries where production often is as small as a few metric tons per year. The strategy would also allow for scheduled, gradual investment in new chemical production facilities without committing to a large production facility from the outset. Ultimately, the large scale manufacturing of individual components and subsequent integration, as done in the electronic and automotive industry, could challenge the traditional centralized economy of scale (*i.e.*, a few large plants) practiced in the chemical industry.

The high heat and mass transfer rates possible in microfluidic systems could allow reactions to be performed under more aggressive conditions and with higher yields than achievable in conventional reactors. More importantly, new reaction pathways deemed too difficult in conventional microscopic equipment may be realized. For example, direct fluorination of aromatic compounds has recently been demonstrated in single, micromachined channels.[6] Even if a microreactor failed, the small quantity of chemicals released accidentally could be easily contained. Moreover, the presence of integrated sensor and control units could allow the failed reactor to be isolated and replaced while other parallel units continued to produce. These inherent safety characteristics suggest that production scale systems of multiple microreactors should enable distributed point-of-use chemical synthesis of chemicals with storage and shipping limitations, such as highly reactive and toxic intermediates.

Microreactor research over the past few years has demonstrated a widening range of chemical applications, increasingly sophisticated designs, and expanding levels of integration. Gas phase reactors tend to be based on microchannel plates or freestanding thin walls from silicon based MEMS fabrication Microchannel systems exploit the high heat transfer rate made possible by the small dimensions and have the additional advantage for chemical production of higher productivity per unit volume than MEMS based devices. Similar to conventional ceramic monolith reactors, however, they suffer from lack of sensing and active control within the microchannel assembly. Stacking of microchannel plates with different reaction and heat

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[10] R. D. Chambers and R. C. H. Spink, "Microreactors for elemental fluorine," *Chem. Comm.* 1999 *10*, 883-884

[11] Lerou, J. J., M. P. Harold, J. Ryley, J. Ashmead, T. C. O'Brien, M. Johnson, J. Perrotto, C. T. Blaisdell, T. A. Rensi and J. Nyquist, "Microfabricated Minichemical Systems: Technical feasibility," *Microsystem Technology for Chemical and Biological Microreactors: Papers of the Workshop on Microsystem Technology, Mainz, 20-21 February, 1995*, DECHEMA, Frankfurt (1996), p. 51

exchanger functions provides the potential for energy integration.[12]

Thin wall reactors offer the opportunity for integration of flow and temperature sensors on the external side. The micron-thick wall provides good thermal contact with the catalyst in the interior. Energy transfer in the active reactor wall may be manipulated by adjusting the thickness of the wall and choosing materials of different thermal conductivity. Thermal isolation is useful when using the thin-wall reactor as a calorimeter, but also creates the potential for multiple steady states for highly exothermic reactions. Increased heat conduction out of the catalyst removes the multiplicity and opens mild reaction conditions typically not accessible in conventional reactors. The integrated heaters and temperature sensors combined with the low thermal mass of the wall has the further advantage of fast thermal response times. The use of a permeable membrane instead of the thin wall allows the integration of separation with chemical reaction, as in macroscopic membrane reactors. For example, the integration of a submicron thickness palladium membrane makes a high efficiency hydrogen purification device and provides the potential for conducting hydrogenation and dehydrogenation reactions.[13]

The small dimensions in microreactor channels imply laminar flow so that mixing occurs primarily by diffusion. This characteristic becomes both a challenge and an advantage for liquid phase reaction systems.[14] To accelerate mixing, most liquid phase reaction systems rely on splitting and recombination of the fluid streams several times to create a laminated fluid with an increased fluid interface and shortened diffusion path.[15] Alternatively, the liquid feed can be introduced in such away as to produce a laminated stream. The choice of design becomes a trade-off between mixing speed, pressure drop, volume flow, and the feasibility of microfabrication. The relatively slow mixing phenomenon can be exploited in phase transfer reactions, separation devices, and nucleation studies as well as in novel microfabrication schemes.[16]

The ability of microfabrication to reproduce complex designs in a parallel fashion should invigorate the innovative nature of reactor design and lessen the tedium of having to chose among particular reactor geometry (*e.g.*, stirred tanks, tubular and trickle bed reactors). In developing microreaction technology, it will be essential to be focused on systems where microfabrication can provide unique process advantages. Such advantages could be derived from increased mass and heat transfer leading to improved yield and safety for an existing process. The real value of the miniaturization effort, however, would be in exploring new reaction pathways and finding economical and environmentally benign solutions to chemical

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[12] Tonkovich, A. L. Y., D. M. Jimenez, J. L. Zilka, M. J. LaMont, Y. Wang and R. S. Wegeng, "Microchannel Chemical Reactors for Fuel Processing," *Process Miniaturization: 2nd International Conference on Microreaction Technology*, New Orleans, LA, (1998), p. 186.

[13] Franz, A., K. F. Jensen and M. A. Schmidt, "Palladium Based Micromembranes for Hydrogen Separation and Hydrogenation/Dehydrogenation Reactions," *Technical Digest 12th International Conference on MicroElectroMechanical Systems*, Orlando, IEEE (1999), p. 382.

[14] Burns, J. R. and C. Ramshaw, "Development of a Microreactor for Chemical Production," *Trans IChemE*, **77**, 206 (1999).

[15] Ehrfeld, W., K. Golbig, V. Hessel, H. Lowe and T. Richter, "Characterization of Mixing in Micromixers by a Test Reaction: Single Mixing Units And Mixer Arrays," *I & EC Research*, **38**, 1075 (1999).

[16] Kenis, P. J. A., R. F. Ismagilov and G. M. Whitesides, "Microfabrication Inside Capillaries Using Multiphase Laminar Flow Patterning," *Science*, **285**, 83 (1999).

manufacturing.

It will be important to exploit characteristics resulting from the small dimensions beyond the high transport rates, specifically forces associated with high surface area to volume ratios. For example, Orchid Biocomputer uses capillary valves and pressure to control fluid deliveries and well volume consistency across multiple reactor wells in combinatorial synthesis.[17] In general, chemical systems rely on large surface areas for separations or reactions. Increases in surface area to volume ratios can be achieved by microfabricating internal structures. Such schemes have been exploited in making separation columns for proteomics, immobilizing enzymes, and size selective catalysis.[18]

The need to develop novel structures with controlled surface characteristics suggests that microreactor fabrication must go beyond classical micromachining and silicon MEMS techniques. Microfabrication in glass already forms the foundation for many biological devices because of the need for an insulating substrate for electrophoresis. Fabrication in plastics using embossing and injection molding techniques is rapidly expanding. The family of chemical self-assembly and microfabrication techniques, "soft lithography," developed by Whitesides and coworkers[19] further provide unique opportunities for microfabrication and chemical tailoring of surfaces to particular applications. Its strengths include the ability to transfer patterns onto non-planar surfaces, formation of microstructures, and compatibility with a wide range of materials: polymers, metals, and ceramics. These techniques have already produced unique microstructures and capabilities that could further advance microchemical systems.

In order for microreactors to move beyond the laboratory into chemical production, they must be integrated with sensors and actuators either on the same chip or through hybrid integration schemes. It was the integrated circuit that created the microelectronics revolution, not the transistor itself. The integration of chemical systems with sensors in μTAS is already a rapid expanding the field and cross-fertilization with microreactors for chemical synthesis will ultimately result in integrated chemical processors. The packaging of multiple reactors presents significant challenges in fluid handling, local reactor monitoring and control not previously addressed in traditional design of chemical plants. Thus, the realization of microreaction technology offers tremendous multidisciplinary research opportunities across biology, chemistry, materials, and electronics, as well as in the traditional chemical engineering sub-disciplines of catalysis, transport phenomena, reaction engineering, and systems.

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[17] DeWitt, S. H., "Microreactors for Chemical Synthesis," *Curr. Opin. Chem. Biol.*, **3**, 350 (1999).

[18] van den Berg, A. and D. J. Harrison (Eds.), *Micro Total Analysis Systems'98*, Kluwer Academic Publishers, Dordrecht (1998).

[19] Xia, Y. N. and G. M. Whitesides, "Soft Lithography," *Ann. Rev. Mater. Sci.*, **28**, 153 (1998).

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8. Acknowledgements

The organizers and participants thanks ARO and DARPA for supporting this workshop. They organizers also thank Ms. Joan Chisholm and Ms. Arline Benford for help in organizing the conference and preparing this report.

9. Appendix -

9.1 Copies of Oral Presentations

Klavs Jensen, MIT	Welcome - Workshop organization and objectives
Wolfgang Ehrfeld Institute for Microfabrication, Mainz, Germany	Microreactor Components and Systems -Basic Properties, Fabrication Methods and Commercial Applications
Mark Burns University of Michigan	Integrated Reaction, Separation, and Detection Systems for Biochemical Analysis
Rolf E. Swenson Orchid Biocomputer	Recent Results of Chemical Syntheses on a Microfluidic Chip
Steve Casalnuovo Sandia National Laboratories	Gas Phase Chemical Detection with and Integrated Chemical Analysis System
Jim Ryley, DuPont Experimental Station	Microchemical System Applications - DuPont Experience
Richard Bellows, Exxon Research and Engineering	Hydrocarbon Fuel Processors - Development Issues in Fuel Cell Vehicle Applications
Anna-Lee Tonkovich Pacific Northwest National Laboratory	Fuel Processing in Microchannel Reactors.
Lanny Schmidt University of Minnesota	Catalytic Partial Oxidation at Millisecond Times
Ian Waitz, MIT	Combustors for Micro Heat Engines
Michele Friedrich Pacific Northwest National Laboratory	Man-portable Microtechnology Based Absorption Heat Pump.

George Whitesides, Harvard University	Microfabrication and Microfluidics Using Polymers and Rapid Prototyping
Martin A. Schmidt MIT	Novel MEMS fabrication approaches
Haim H. Bau University of Pennsylvania	Microfluidic Systems Fabricated in Low Temperature Co-fired Ceramic Tapes
Lawrence H. Dubois, DARPA/DSO	Mesoscopic Machines - There is plenty of room in the middle!"

9.2 Appendix - Copies of Working Group Presentations

I: *Opportunities for Microenergy Devices,* Moderator: Robert Wegeng, PNNL

II: *Challenges and Needs in Microfabrication and Materials,* Moderator: Martin Schmidt, MIT

III: *Chemical Applications of Microchemical Systems*, Moderator: Klavs Jensen, MIT

9.3 Appendix - Copies of Poster Presentations

Presenter	Title
Jeffrey G. Killian Johns Hopkins University	Developing Conducting Polymers for Charge Storage Applications
Brian K. Paul Oregon State University	Microlamination for Microtechnology-Based Energy and Chemical Systems
Xiang Zhang Pennsylvania State University	Microfabrication of Truly 3D Complex Microstructures with Materials Beyond 1C Processes (copy not available)
L. James Lee Ohio State University	Fabrication Techniques for Polymer Based Microfluidic Devices
Debra R. Rolison	Using Nanoscale Mesoporous Architectures to Design

Naval Research Laboratory	Integrated Fuel Cell Catalysts or Pave High Surface Areas with Nanowires
John N. Harb, Brigham Young University	Microbatteries for Use with MEMS Devices
Mark R. Holl University of Washington	A Microfluidic Sample Preconditioning System for CBW Agent Detection and Quantification
Nitish V. Thakor Johns Hopkins University	VLSI Electrochemical Sense Array for Chem/Bio/Neuro
Anil R. Oroskar UOP	Process Intensification Needs in Petroleum & Petrochemical Industry
Eduardo E. Wolf University of Notre Dame	Microfabricated Bimetallic Catalysts for the Hydrogenation of Croton Aldehyde
Goran Jovanovic Oregon State University	A Microtechnology Based Chemical Reactor System for Catalytic Dechlorination of Chlorinated Solvents
Rebecca Jackman, MIT	Liquid Phase and Multi Phase Microreactors for Chemical Synthesis
Aleks Franz, MIT	High Temperature Gas Phase Catalytic and Membrane Reactors
Patrick L. Mills DuPont Central Research & Development	Microfabricated Gas-Phase Reactor: Scale-Up & Packaging
Louis C. Chow University of Central Florida	Mesoscale Refrigerator
Haim Bau University of Pennsylvania	Microfluidic Components and Systems Fabricated in Low Temperature Co-fired Ceramics Tapes (see Haim Bau - Presenatation)
Anantha Krishnan	Computational Design Tools for Micro-Chemical Systems

Microchemical Systems and Their Applications

Sponsored by:
Army Research Office (ARO)
Defense Advanced Research Projects Agency (DARPA)

Organizing Committee:

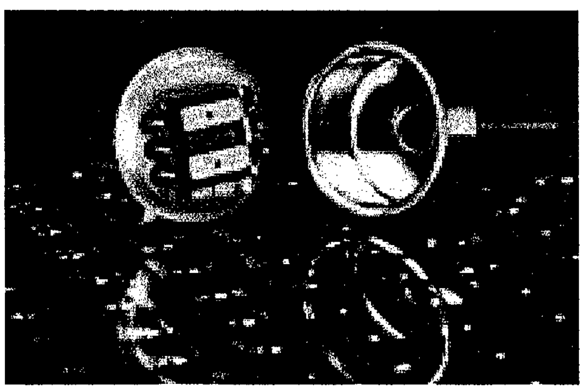
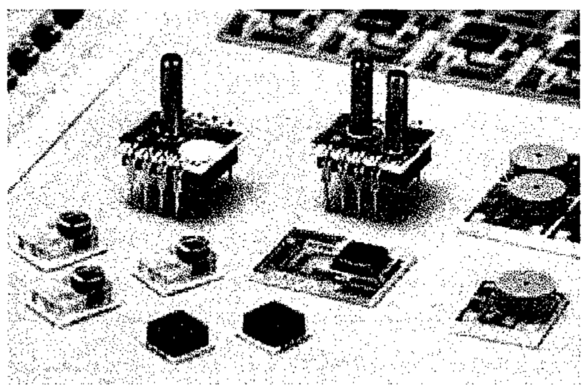
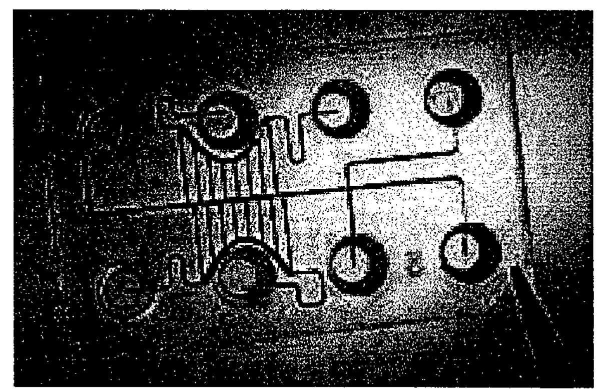
Peter Fedkiw ARO/North Carolina State University
Klavs Jensen MIT
Robert Nowak DARPA
Richard Paur ARO

Workshop Objectives

- Review the state-of-art in microchemical systems, with emphasis on microreactor systems for chemical and energy generation applications, including:
  - Fuel processing for hydrogen generation and fuel cells
  - Thermal power sources (microengines, heat pumps, thermoelectric and thermophotovoltaic devices)
  - Synthesis of chemical compounds
- Identify and evaluate:
  - Applications for which microreactors have potential
  - Fabrication techniques that incorporate metals, polymers, and ceramics, beyond standard silicon-based MEMS processes
  - Integration of microreactors with other unit operations, sensors, and actuators
  - Challenges for realization of microreaction technology

MEMS TECHNOLOGY

- MEMS = MicroElectroMechanical Systems
  - Use of microfabrication techniques from semiconductor processing to make small electromechanical devices, including
    - pressure sensors, valves, pumps, accelerometers, ...
  - Increasing use of materials beyond silicon
    - polymers, glass, ceramics
  - Rapid growth in biological applications
    - DNA sequencing - Genome project
    - PCR, capillary electrophoresis, cell sorting
  - Emerging interests in microchemical/energy applications

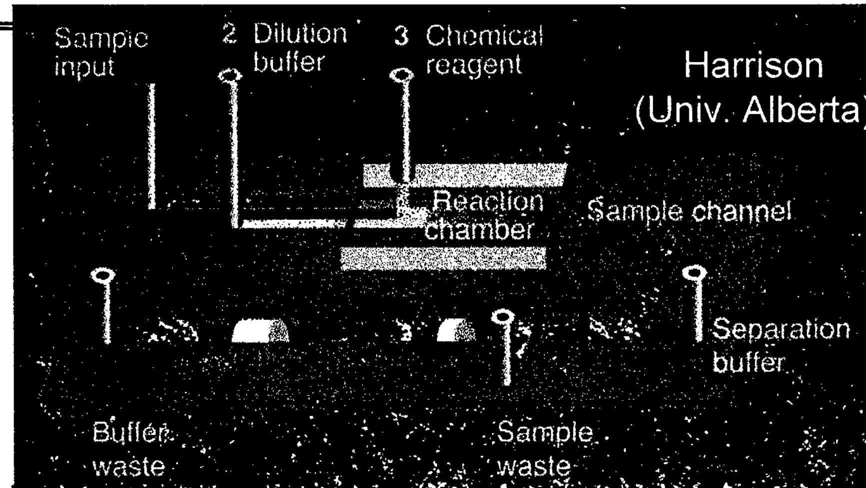
ARO/DARPA *Workshop Microchemical Systems and Their Applications*

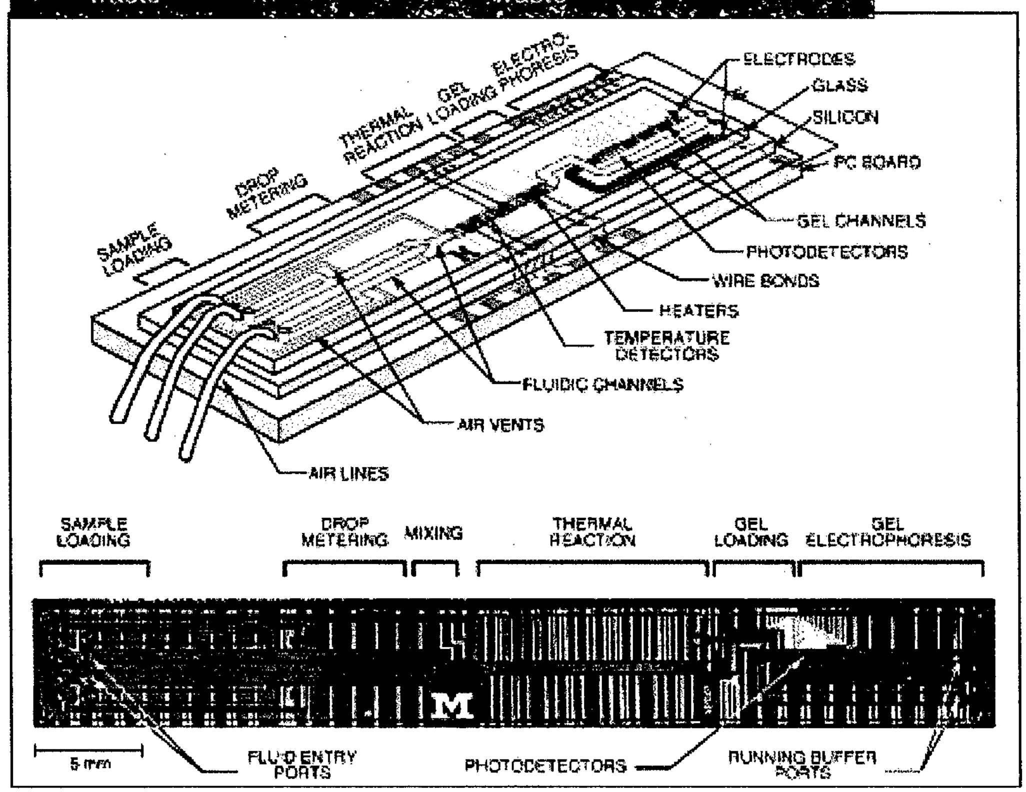
μTOTAL ANALYSIS SYSTEMS - “LABORATORY ON A CHIP”

- Drug discovery
- Clinical diagnostics

- Advantages:
  - Small volumes
  - Parallel operation
  - Fast screening

- Examples:
  - Enzyme inhibition
  - DNA/RNA separation and sequencing
  - Receptor ligand binding
  - Immunoassay





Burns *et al.* *Science*, **282**, 484 (1998)

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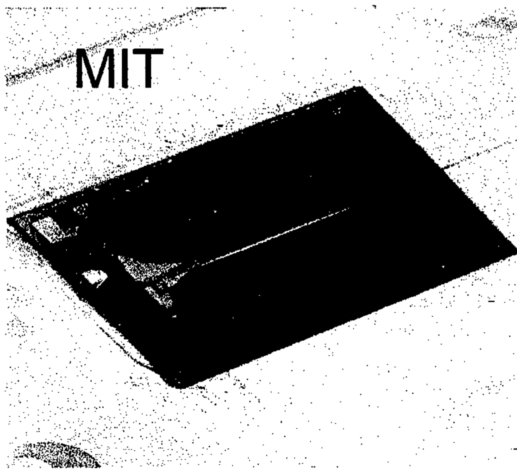
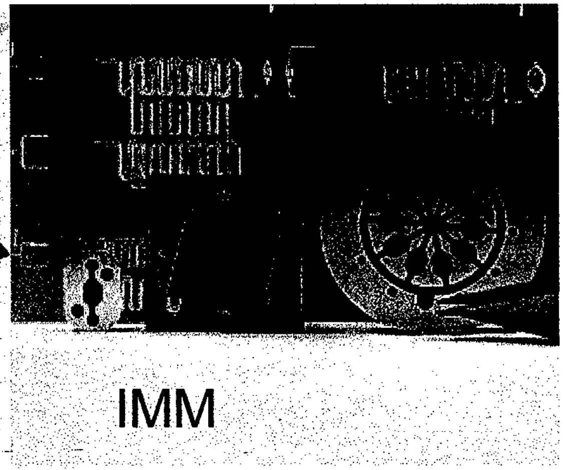
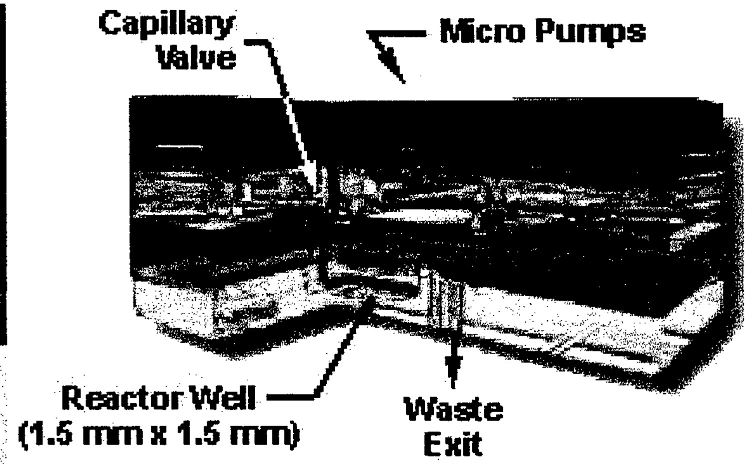
Microchemical Systems - Motivation







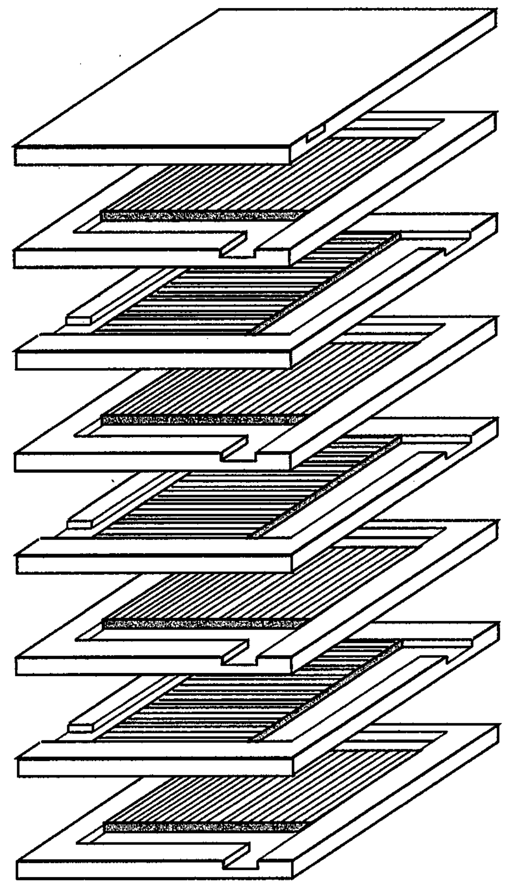
Orchid Biocomputer.

- Potential advantages:
  - High throughput reaction/catalyst screening - combinatorial chemistry
  - Integration of sensors and actuators
  - Improved chemical performance - operation in small dimensions
  - Improve heat and mass transfer - fast thermal cycles
  - Distributed manufacturing - on demand production of toxic intermediates
  - Fast scale-up to production by replication

ARO/DARPA *Workshop Microchemical Systems and Their Applications*

Microchemical Energy Systems - Motivation

- Energy devices:
  - Liquid fuel processing for hydrogen fuel cells
  - Cooling/heating
  - Heat pumps
  - Portable - man portable energy source
  - Space applications
  - Air purification
  - Integration with other electrical and mechanical devices



PNNL fuel processing unit

Working Group I: Opportunities for Microenergy Devices

- Moderator: Robert Wegeng, PNNL
  - Fuel processing (partial oxidation, hydroforming, catalysts)
  - Intake and exhaust conditioning
  - Converter technology (TPV,TE, Fuel Cells, Microturbines)
  - Microfluidics (pumps, valves, integration)
  - Energy integration
  - Systems integration and packaging

Working Group II: *Challenges and Needs in Microfabrication and Materials*

- Moderator: Martin Schmidt, MIT

  - Materials for high temperature, corrosive environments
  - Microfabrication approaches for ceramics, metals, polymers
  - Fabrication and materials challenges in packaging
  - Integration of sensors, actuators, and chemical components
  - Cost, rapid prototyping, robustness, lifetime testing
  - Compatibility with IC processing

Working Group III: Chemical Applications of Microchemical Systems

- Moderator: Klavs Jensen, MIT
  - Opportunities for chemical synthesis, novel applications
  - Advantages of microscale synthesis
  - Speed up of process development - laboratory, combinatorial chemistry
  - Integration with separation and other unit operations
  - Analytical application, integration with micro total analysis systems
  - Barriers to implementation, commercialization

Microchemical Systems and Applications

7:20 pm - 8:00 pm	Microreactor Components and Systems -Basic Properties, Fabrication Methods and Commercial Applications	Wolfgang Ehrfeld Institute for Microfabrication, Mainz, Germany
8:00 pm - 8:40 pm	Integrated Reaction, Separation, and Detection Systems for Biochemical Analysis	Mark Burns University of Michigan
8:40 pm - 9:20 pm	Recent Results of Chemical Syntheses on a Microfluidic Chip	Rolf E. Swenson Orchid Biocomputer
9:20 pm - 10:00 pm	Gas Phase Chemical Detection with and Integrated Chemical Analysis System	Steve Casalnuovo Sandia National Laboratories

Chemical and Fuel Processing

8:00am - 8:40am	Microchemical System Applications - DuPont Experience	Jim Ryley, DuPont Experimental Station
8:40am - 9:20am	Hydrocarbon Fuel Processors - Development Issues in Fuel Cell Vehicle Applications	Richard Bellows, Exxon Research and Engineering
9:20am - 10:00am	Fuel Processing in Microchannel Reactors.	Anna-Lee Tonkovich Pacific Northwest National Laboratory
10:00 am - 10:30 am	*Break*	
10:30am - 11:10 am	Catalytic Partial Oxidation at Millisecond Times	Lanny Schmidt University of Minnesota
11:10am - 11:50 am	Combustors for Micro Heat Engines	Ian Waitz, MIT
11:50am - 12:30 am	Man-portable Microtechnology Based Absorption Heat Pump.	Michele Friedrich Pacific Northwest National Laboratory

Materials and Microfabrication

1:30pm - 2:20 pm	Microfabrication and Microfluidics Using Polymers and Rapid Prototyping.	George Whitesides, Harvard University
2:20pm - 3:00 pm	An Increasingly Novel Technology for MicroChemical Systems: Silicon Micromachining	Martin A. Schmidt MIT
3:00pm - 3:40 pm	Microfluidic Systems Fabricated in Low Temperature Co-fired Ceramic Tapes	Haim H. Bau University of Pennsylvania

Posters - Dinner - Workgroups

- 3:30pm - 6:00pm: Coffee Break, Poster Session, and Informal Discussions
- 6:00pm - 7:00pm: Initial Meeting of Working Groups
- 7:00pm - 8:30 pm: Dinner, Ballrooms B&C
  - Speaker: Lawrence H. Dubois, DARPA/DSO
    "Mesoscopic Machines - There is plenty of room in the middle!"

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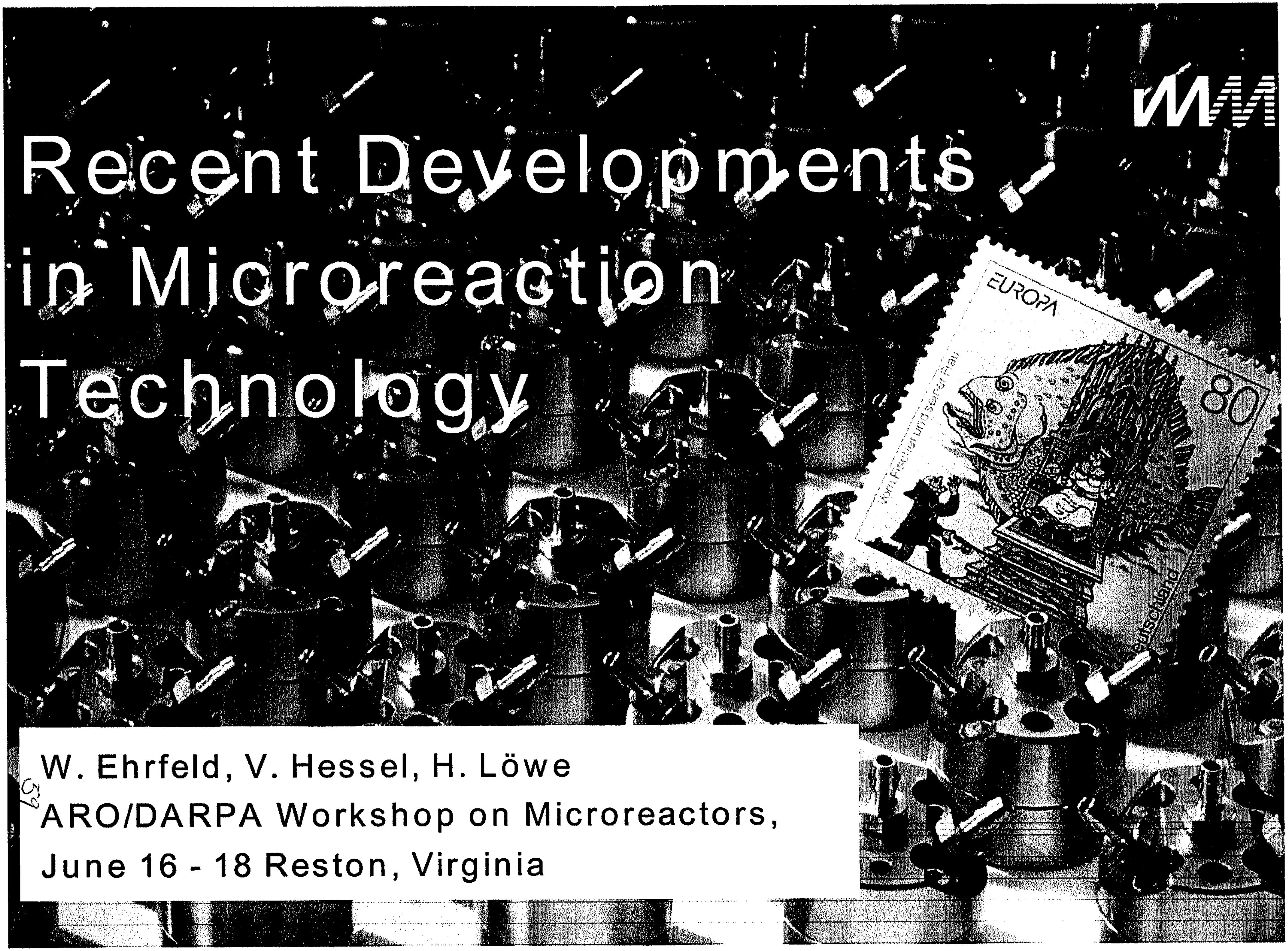
Friday June 18

- 8:00am - 12:30pm: Working Groups
- 12:30pm - 2:00pm
- 2:00pm - 3:30pm: Plenary session - Summaries
- 3:30pm: Adjourn



Recent Developments in Microreaction Technology

W. Ehrfeld, V. Hessel, H. Löwe

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ARO/DARPA Workshop on Microreactors,

June 16 - 18 Reston, Virginia

OUTLINE

Todays applications of microreactors

- Heat transfer
- Mixing
- Emulsion generation
- Gas / liquid contacting

Commercialization of microreactors

- Micromixers
- Liquid / liquid microreactor
- Micropumps
- Nano titer plates

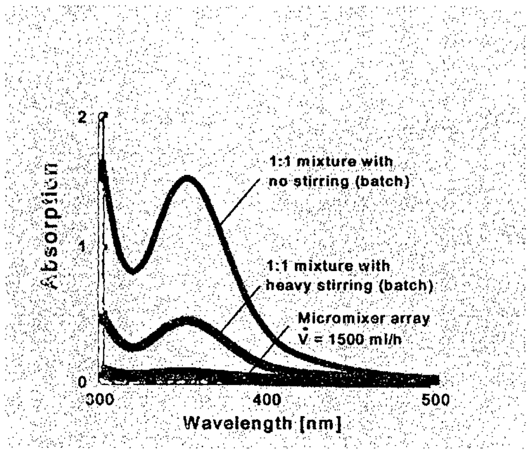
Recent microreactor developments

- Molecular biotechnology
- Catalyst screening
- Multiphase processing
- Gas phase reaction technology
- Electroorganic synthesis

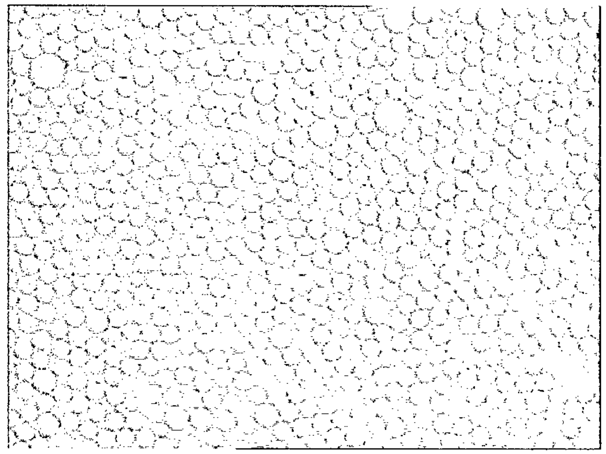
FUNDAMENTAL PROPERTIES OF MICROREACTORS

Physical Size

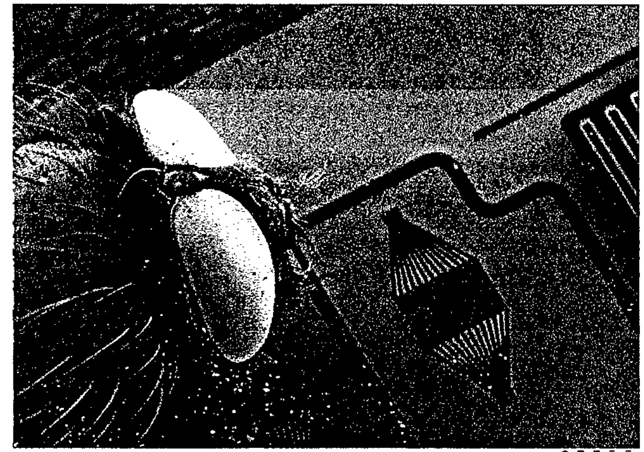
Decrease in linear dimensions



Increase in surface area to volume ratio

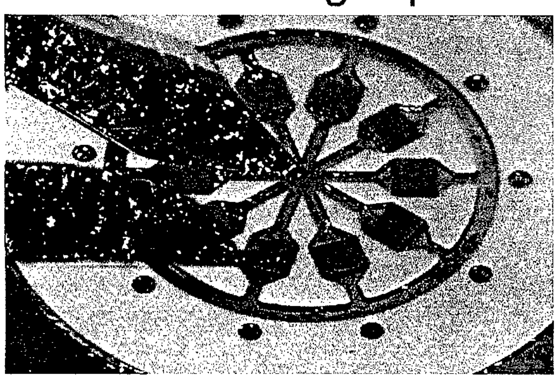


Decrease in volume

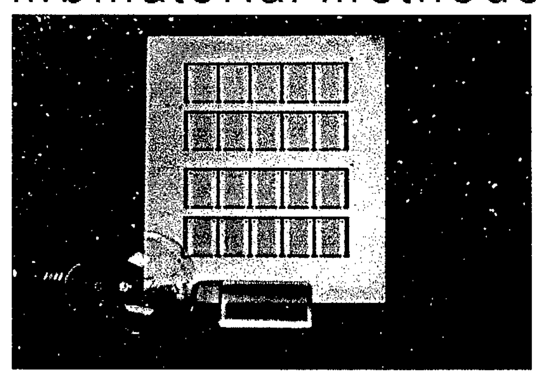


Number of Units

Parallel operation: Numbering-up



Screening based on combinatorial methods



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APPLICATION FIELDS OF MICROREACTORS

Process development

Extremely wide range of operation conditions

Faster transfer of research results into production

Production

Higher flexibility to a varying production demand

Higher process flexibility by using a LEGO system

Cost reduction by series manufacturing

WE / VH 80333c

APPLICATION FIELDS OF MICROREACTORS

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Distributed Production

Production on-demand

Reduction of storage and transport expenditure

Fast official approval

Safety

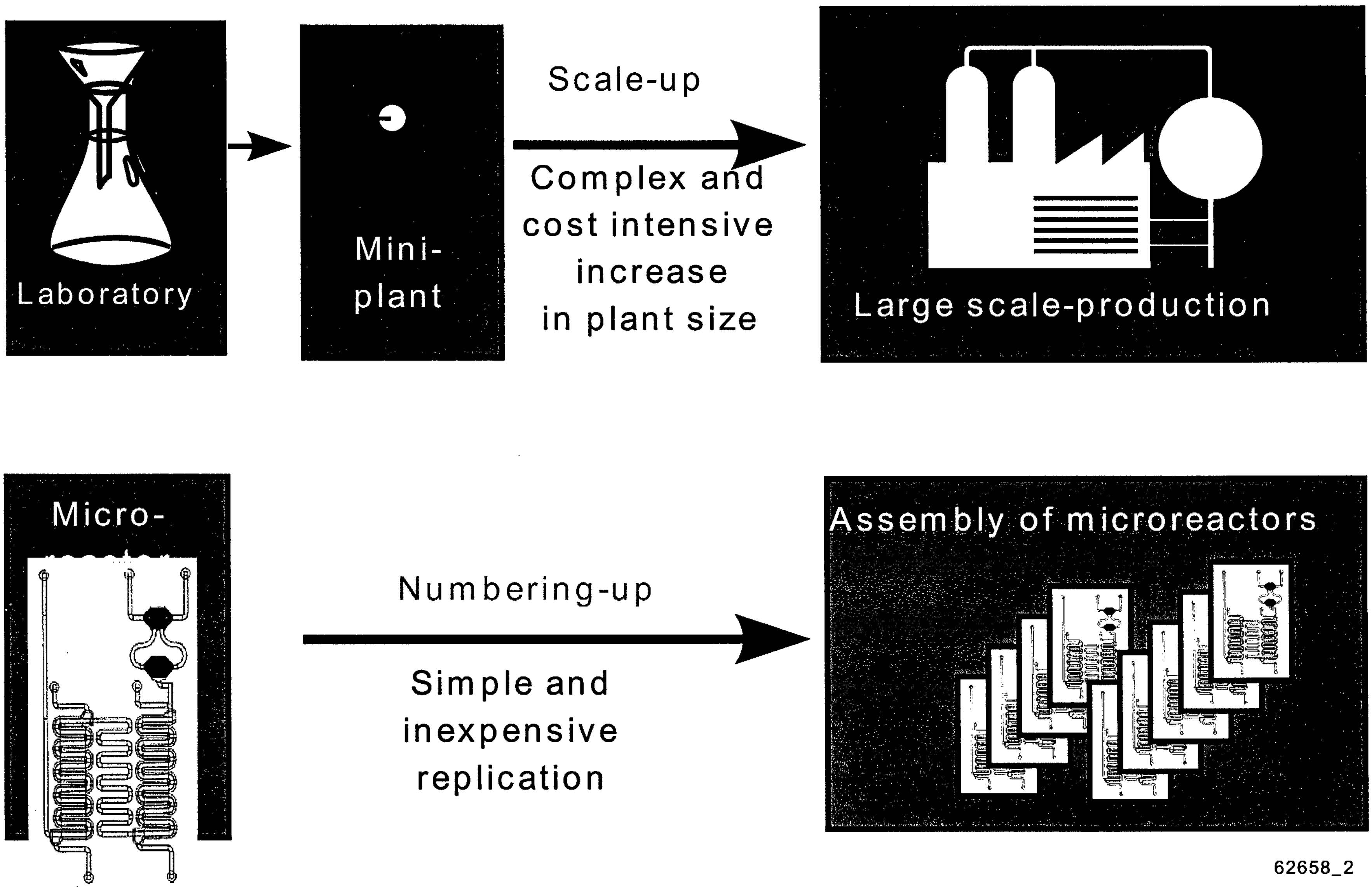
Small hold-up

Flame arrestor effect

Improved process control by short response times

WE / VH 80335c

SCALE-UP OF CHEMICAL REACTORS



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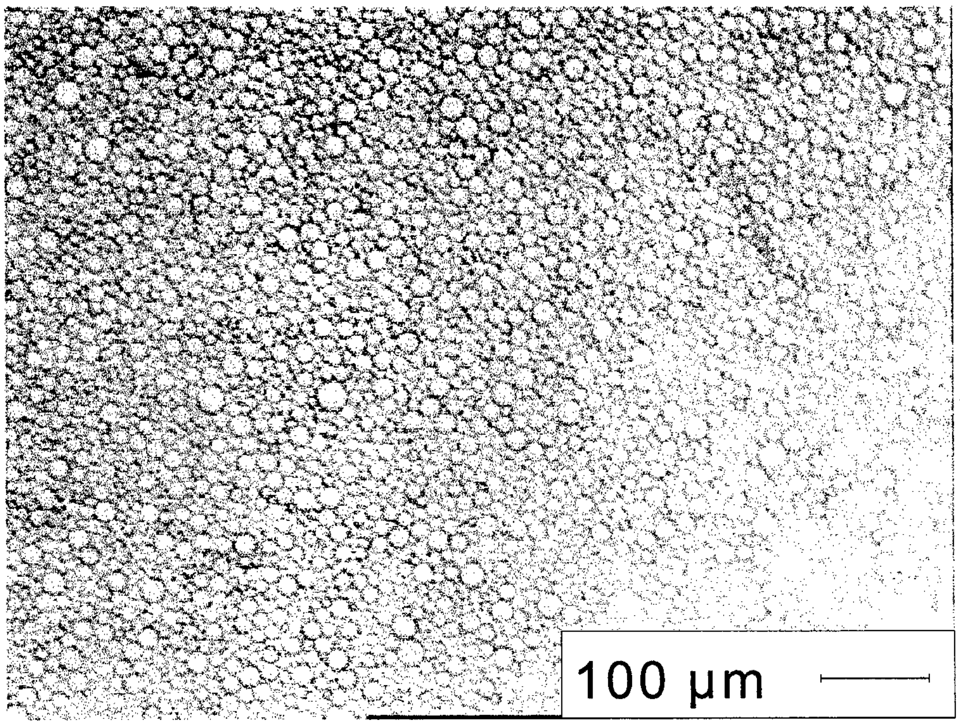
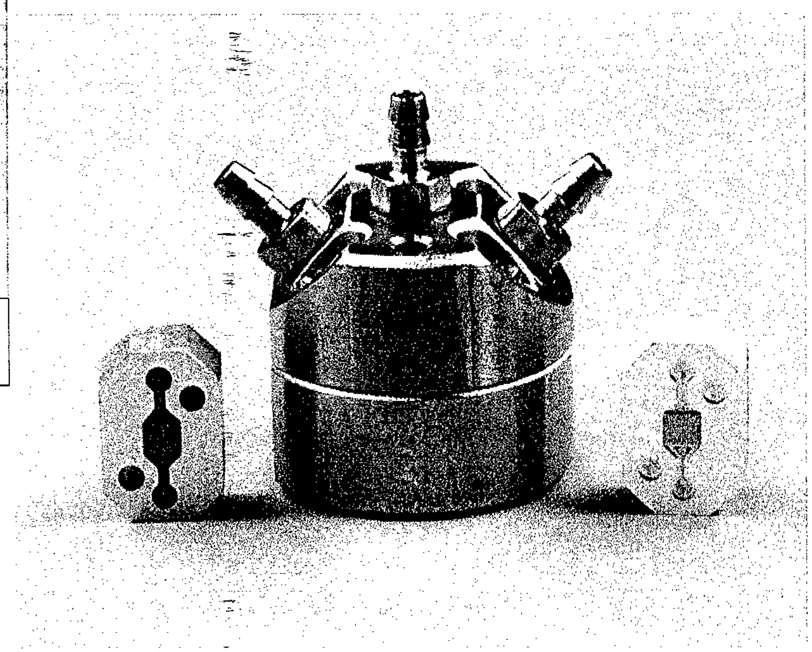
GENERATION OF SMALL DROPLETS IN A MICROMIXER



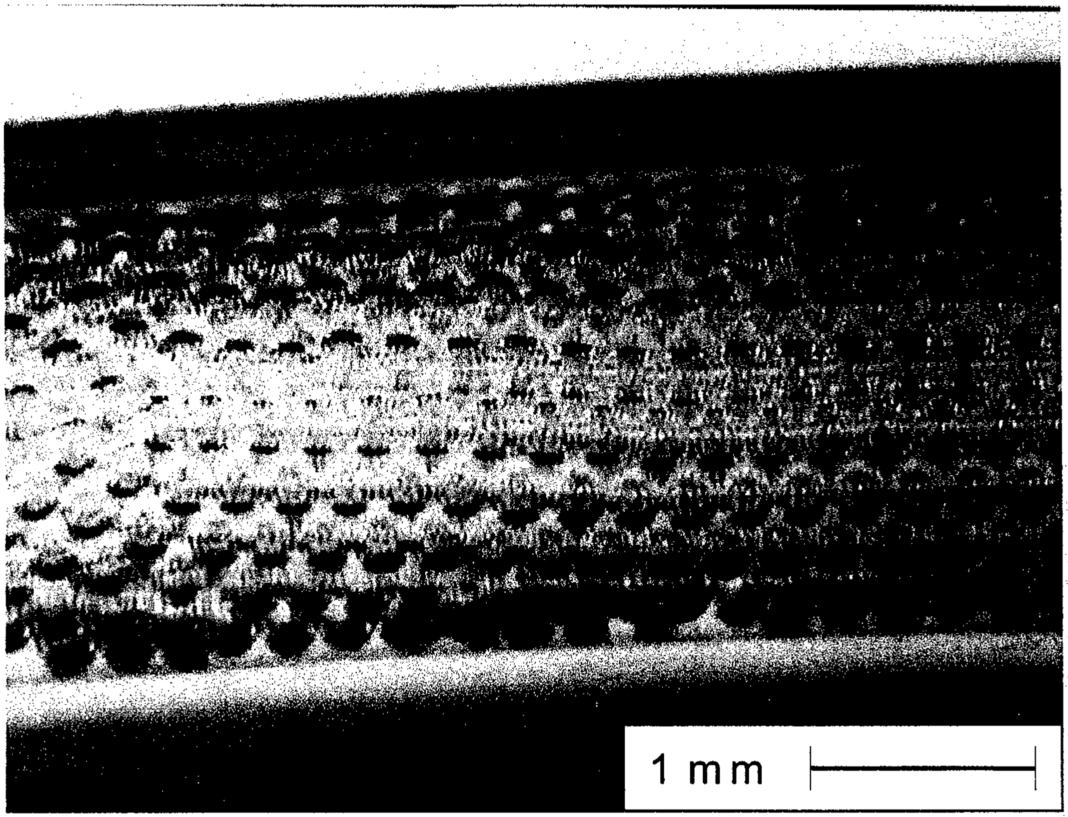
- Fresenius Journal of Analytical Chemistry, accepted (1999)



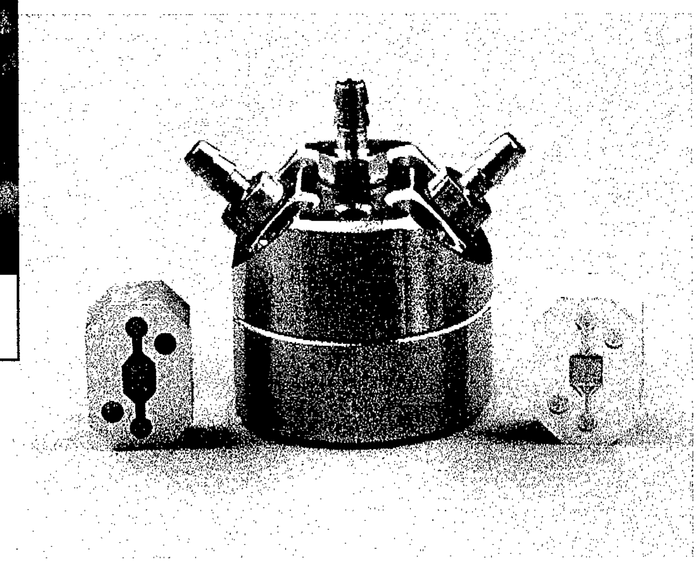
Increase in surface to volume ratio

VH/LA E80486b

GENERATION OF SMALL GAS BUBBLES IN A MICROMIXER



- Proceedings of 2nd Int. Conference on Micro-reaction Technology, 259 (1998)

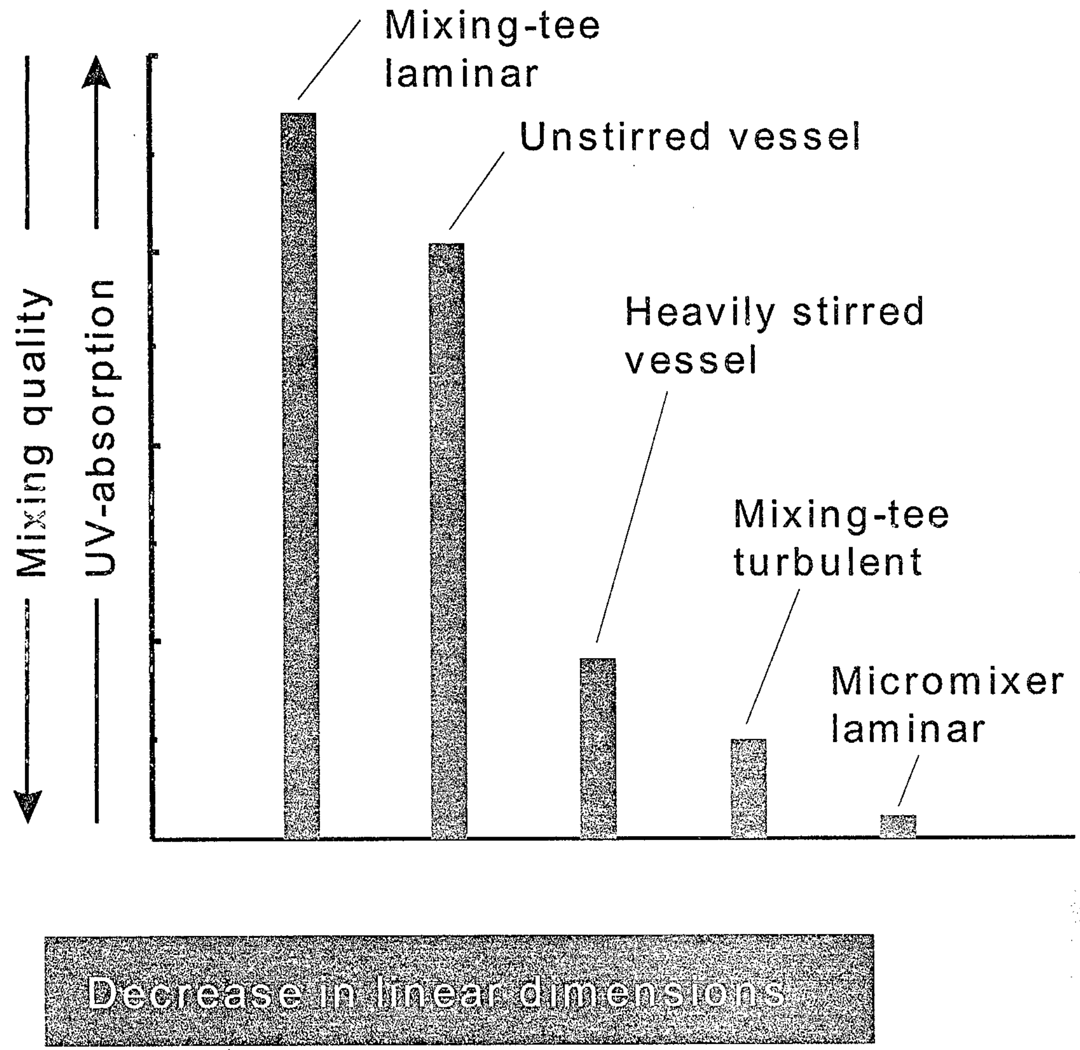


Increase of surface to volume ratio

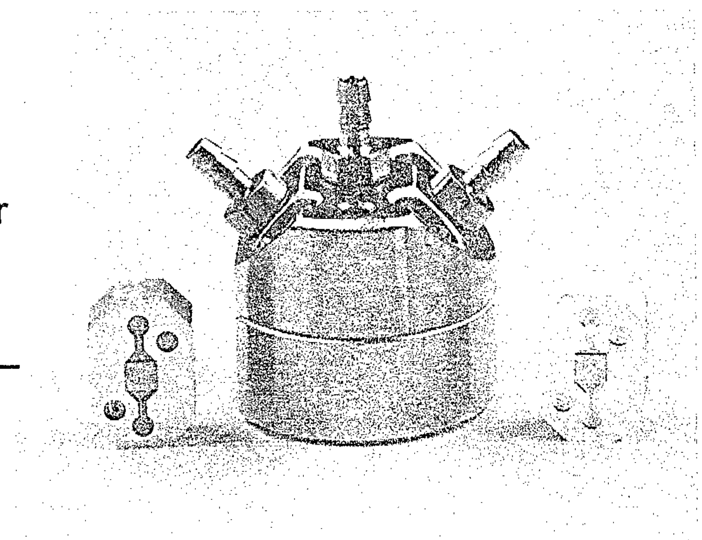
VH / LA 64606b

66

ULTRAFAST MIXING IN MICROMIXERS



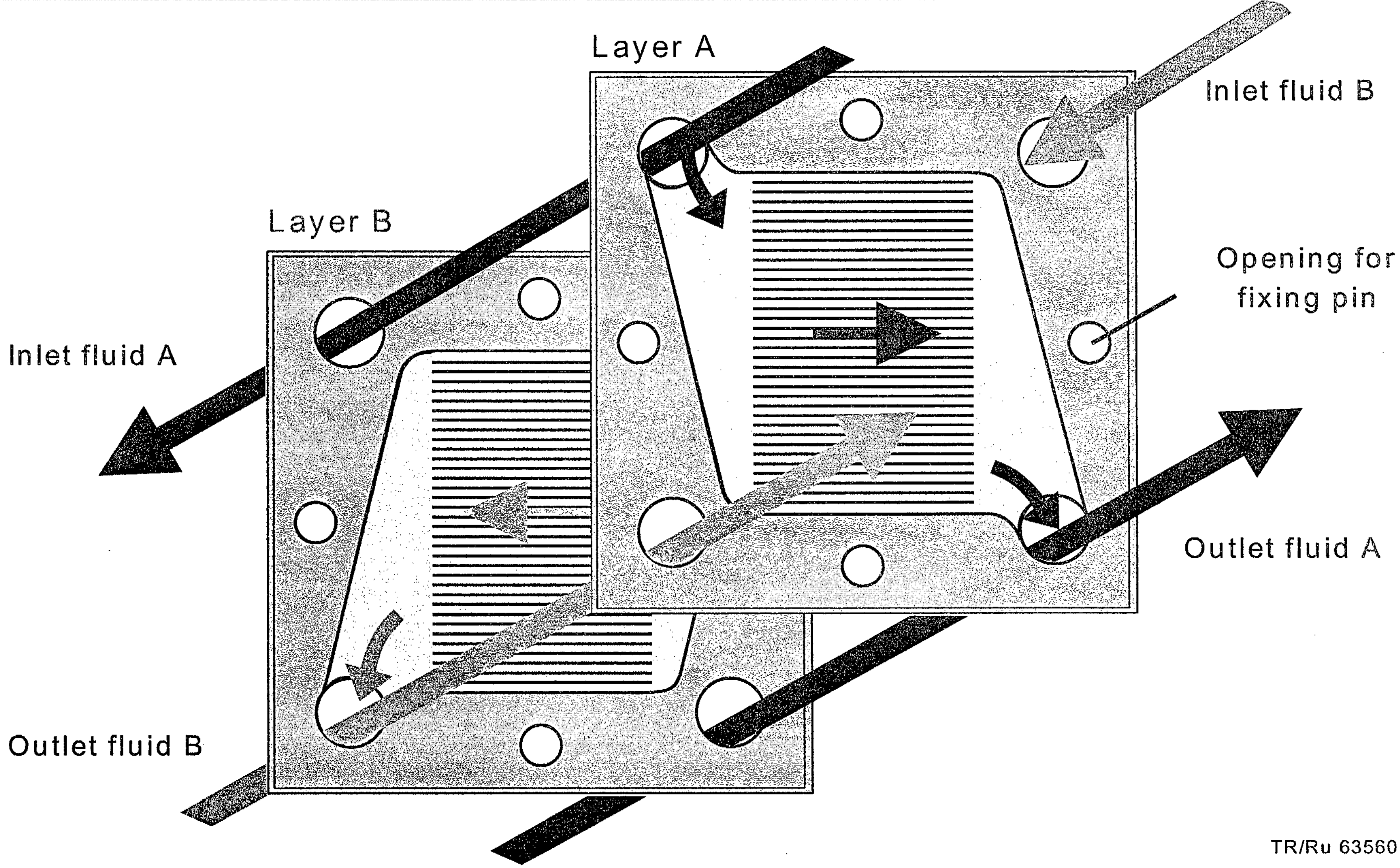
- Ind. Eng. Chem. Res. March Issue (1999)



VH / LA 63821c

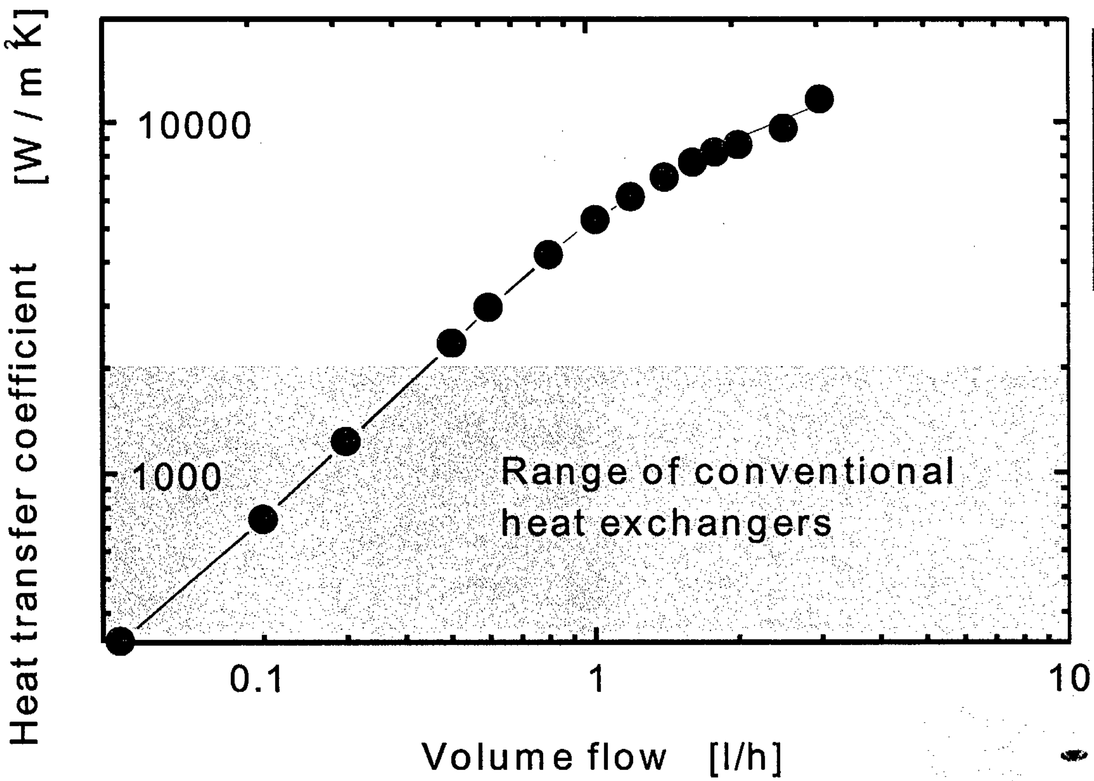
67

HEAT EXCHANGER WITH COUNTERCURRENT FLOW: MASK LAY-OUT



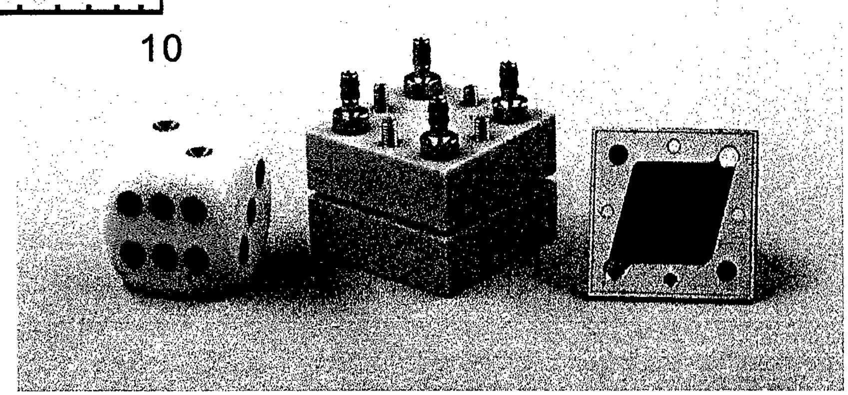
TR/Ru 63560

HIGHLY EFFICIENT HEAT TRANSFER IN MICRO HEAT EXCHANGERS



- Ullmann's Encyclopedia of Industrial Chemistry, Chapter: Microreactors, 6th edition (1999)

Layer thickness: 100 µm

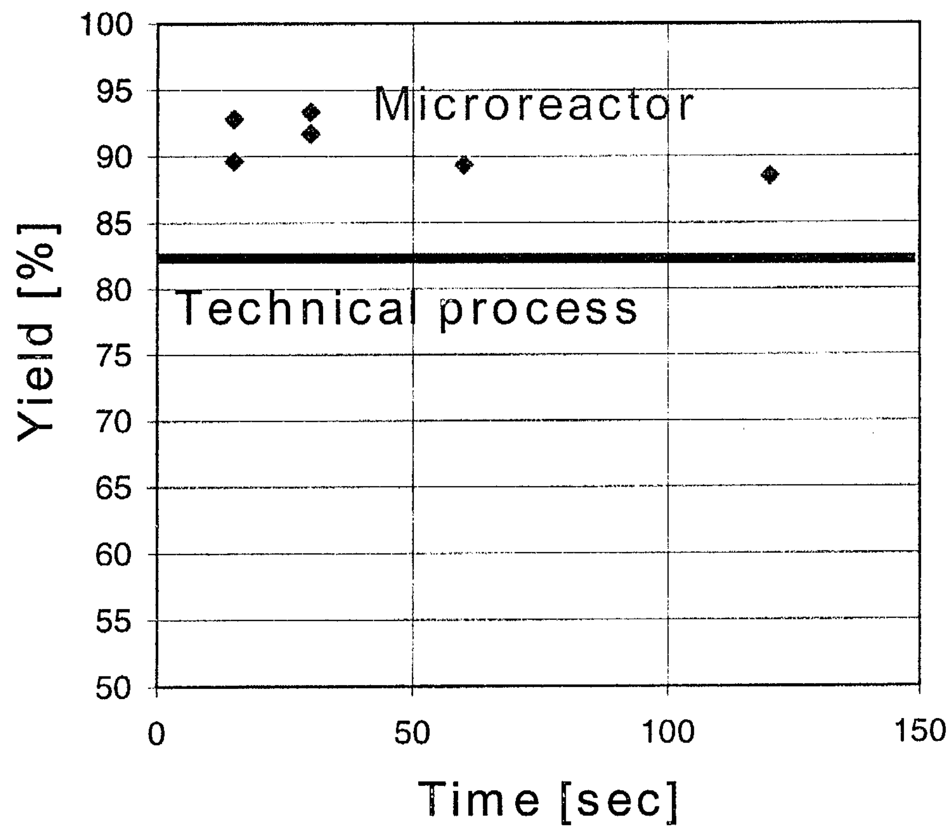


Decrease of linear dimensions

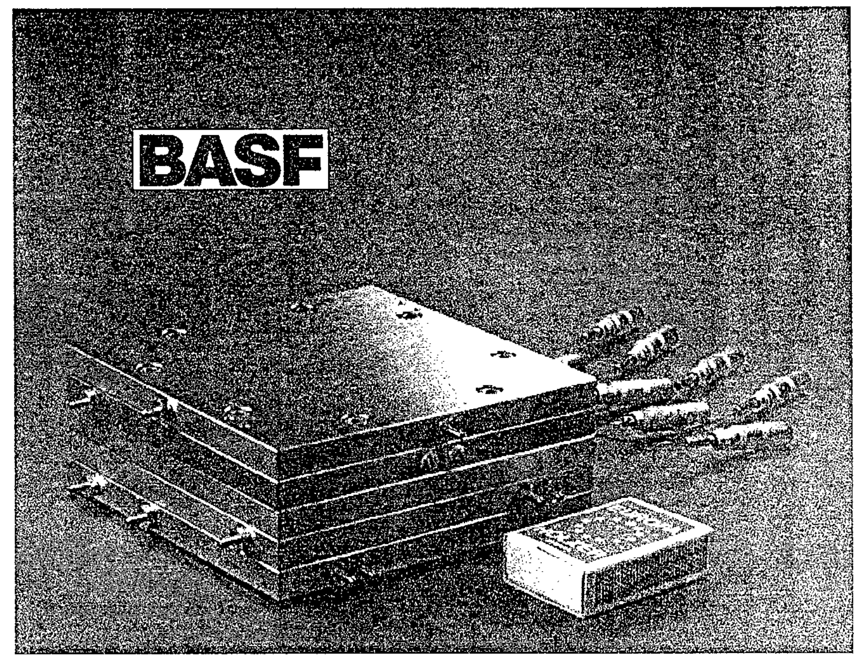
VH / LA 64316b

69

ISOTHERMAL OPERATION BY EFFICIENT HEAT TRANSFER IN A LIQUID/LIQUID MICROREACTOR



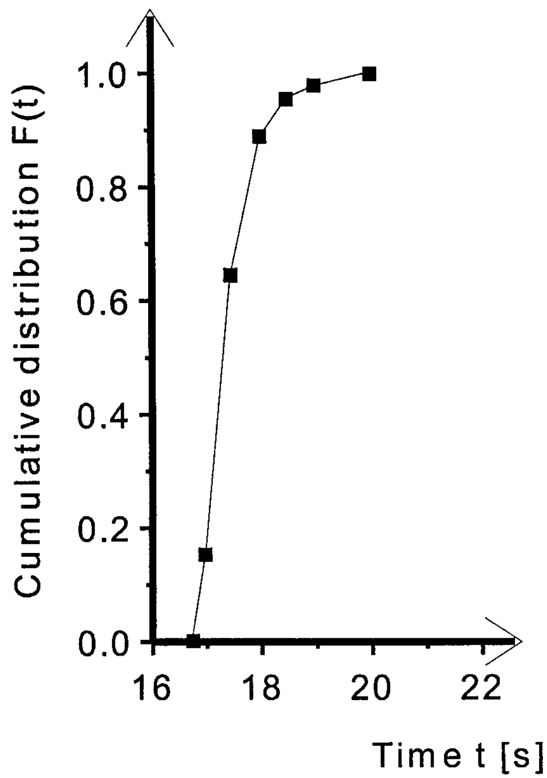
- Proceedings of 2nd Int. Conference on Micro-reaction Technology, 183 (1998)



Decrease in linear dimensions

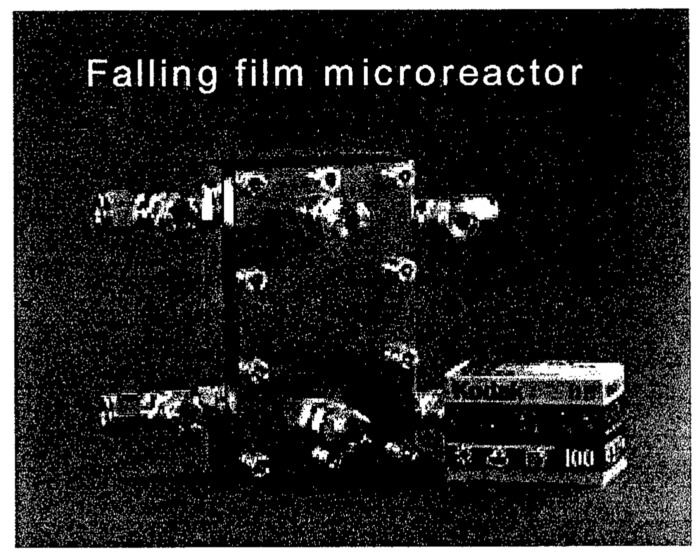
VH/LA 80167b

RESIDENCE TIME DISTRIBUTION OF PARALLELY OPERATED MICROCHANNELS



Parallel operation

- Proceedings of the 3rd Intern. Conference on Microreaction Technology, to be published (1999)



Falling film microreactor

VH/LA 90202

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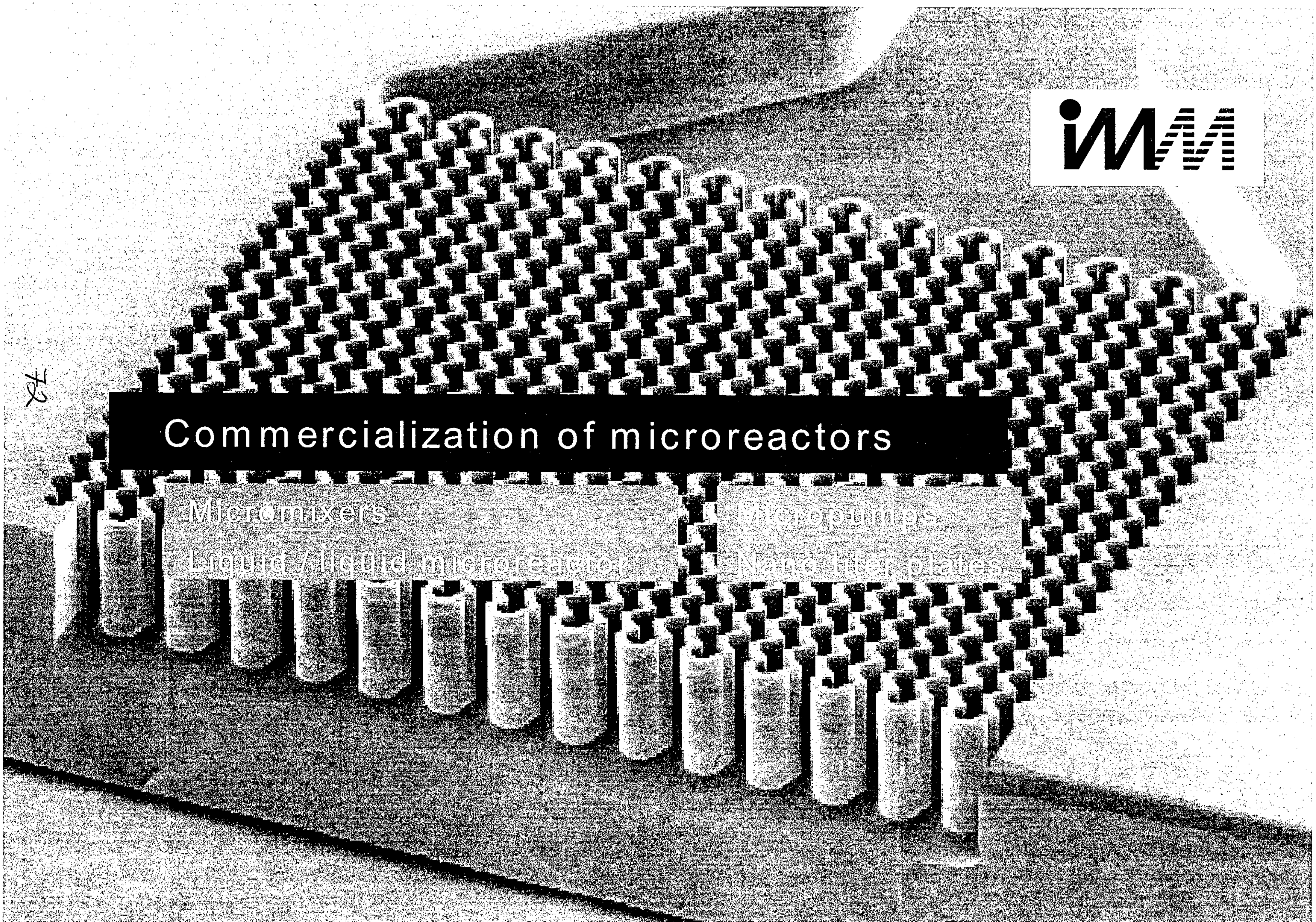
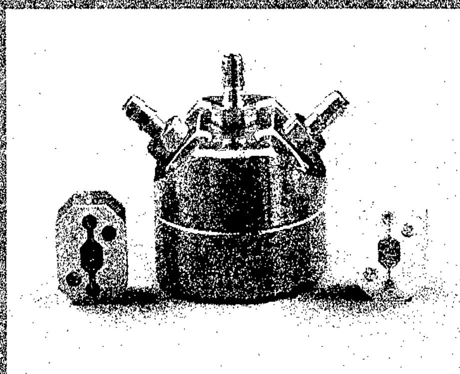
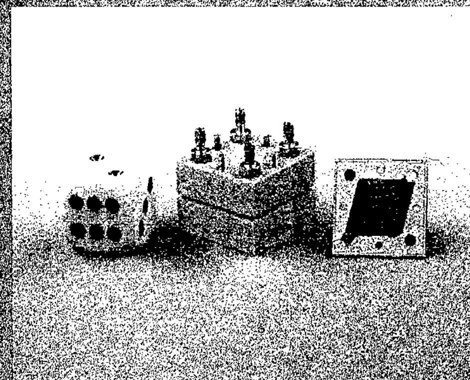
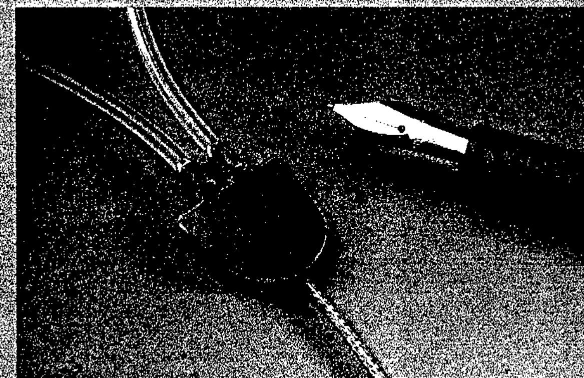
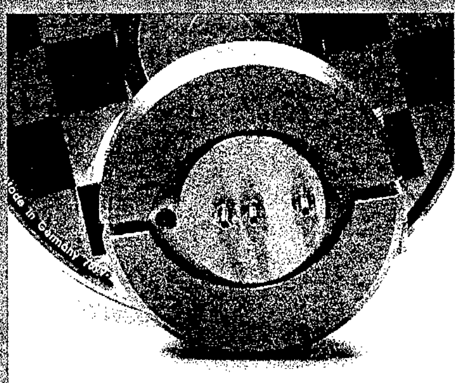

Commercialization of microreactors
Micromixers
Liquid / liquid microreactor
Micropumps
Nano titer plates

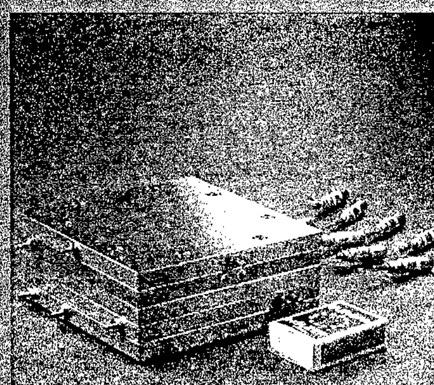
SMALL SCALE PRODUCTION FOR MICROREACTION TECHNOLOGY

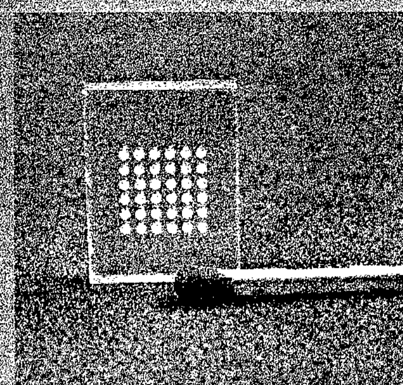

Micromixers

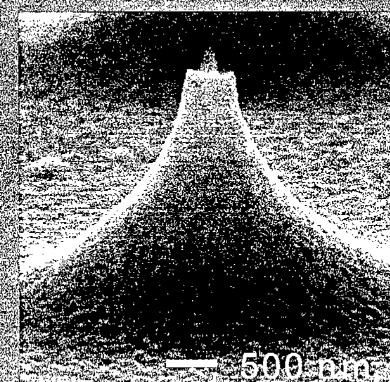

Heat exchangers


Micropumps


Micromixer arrays

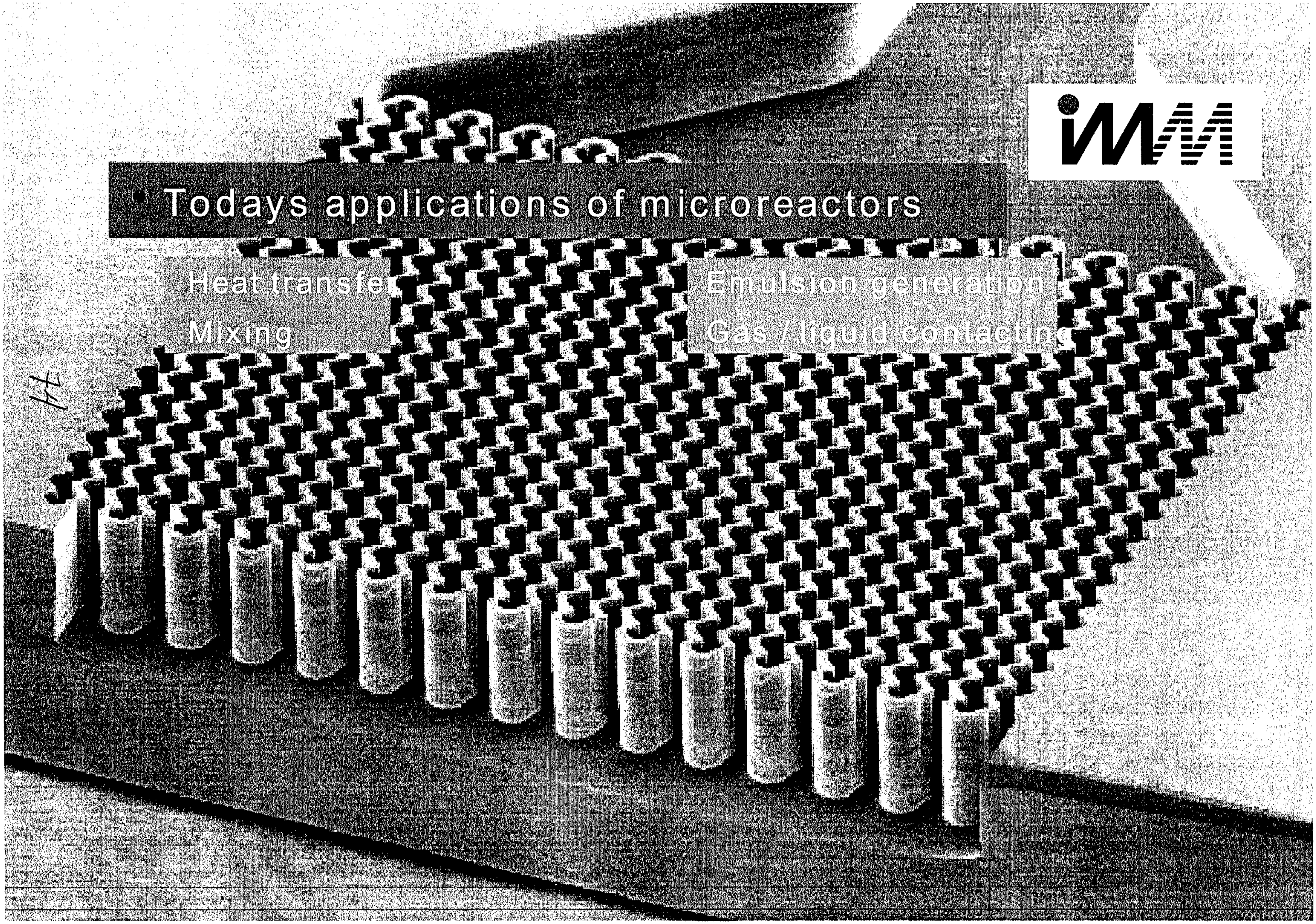

Microreactors


Microtiter plates

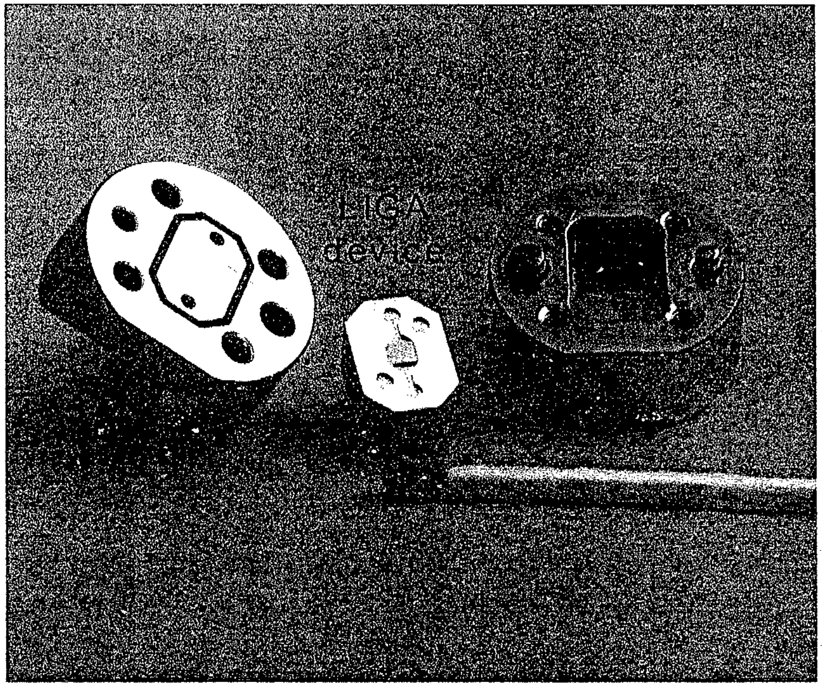


SNOM-tips

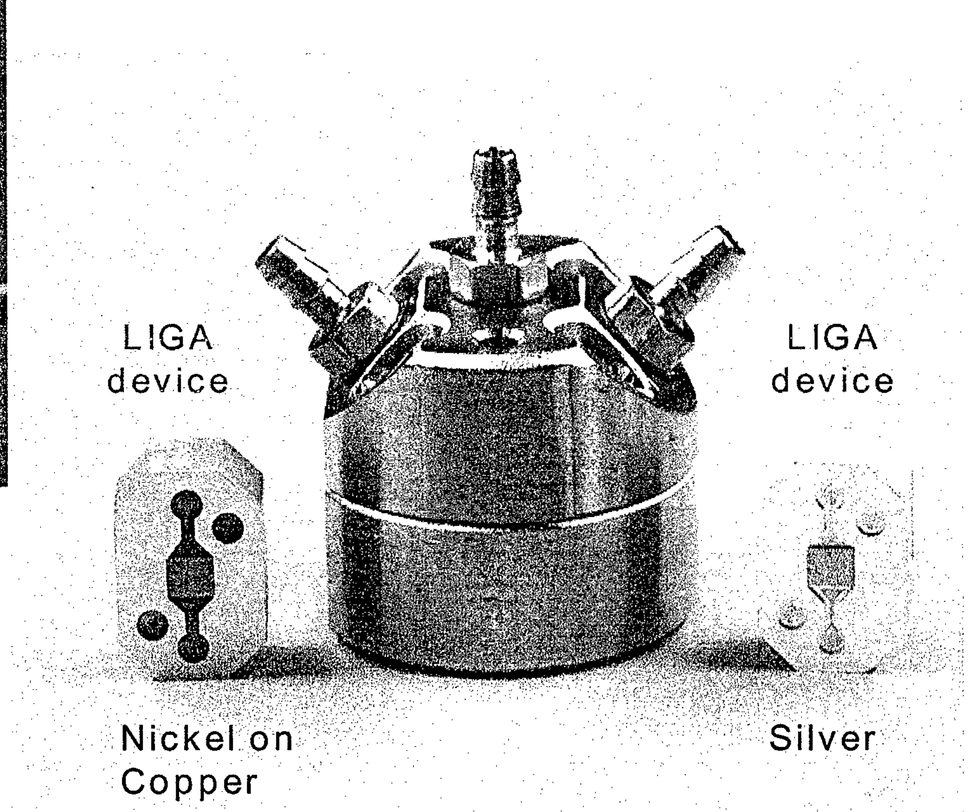
E 80493 TR


Todays applications of microreactors
Heat transfe
Mixing
Emulsion generation
Gas / liquid contactin

LIGA MICROMIXER



Devices on the market



- LIGA technique
- Nickel, Nickel on copper, Silver
- Channel width: 25, 40 μm

VH/ LA 64526b

MICROMIXING ELEMENT

Devices on the market

500 µm

100 µm

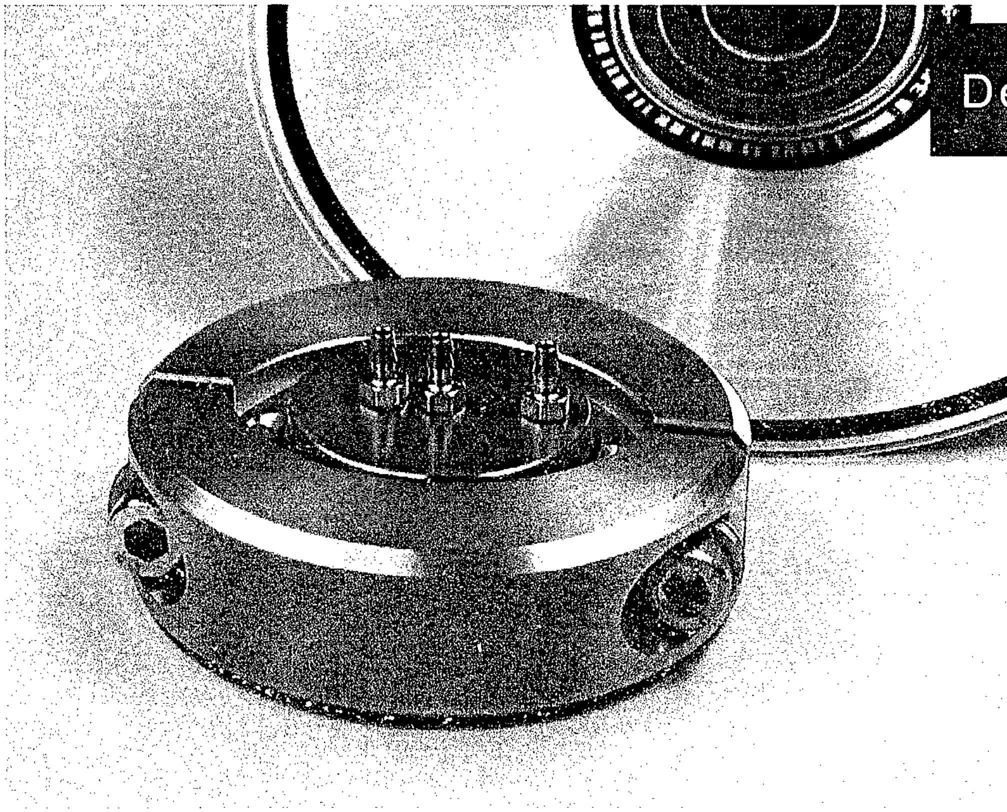
- LIGA technique
- Nickel, Nickel on copper, Silver
- Channel width: 25, 40 µm

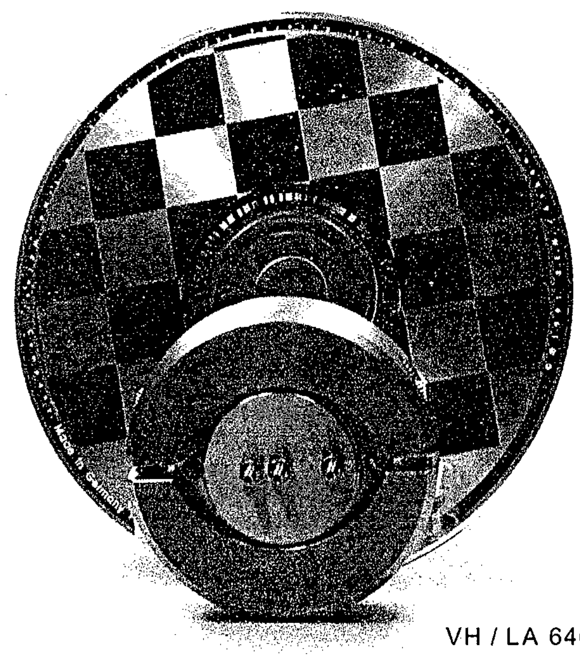
VH / LA 64528b

76

MICROMIXER ARRAY WITH TEN PARALLEL OPERATING MIXING ELEMENTS

Devices on the market





- LIGA technique
- Nickel, Nickel on copper, Silver
- Channel width: 25, 40 μm

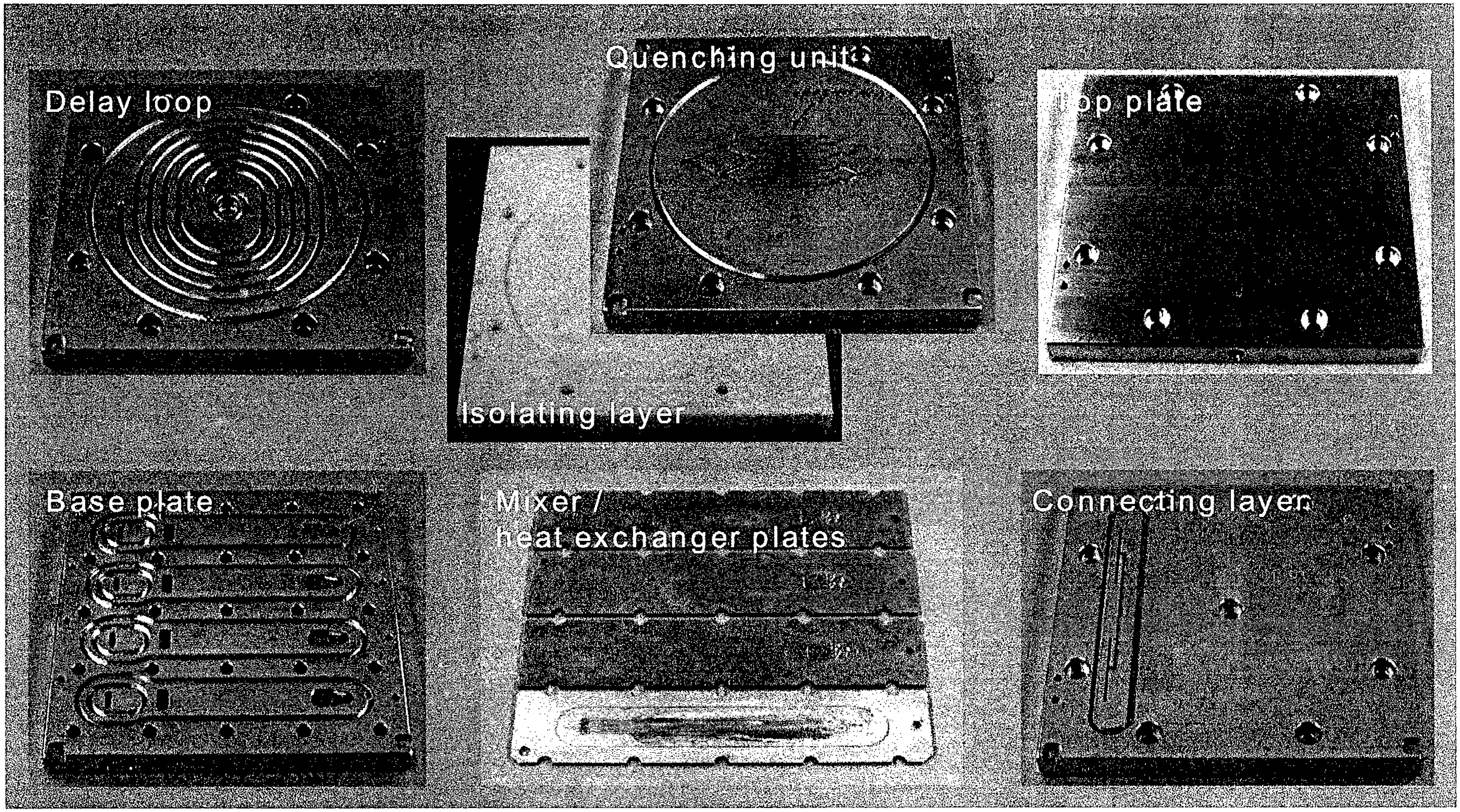
VH / LA 64697b

LIQUID / LIQUID PHASE MICROREACTOR WITH MODULAR ASSEMBLY

Devices on the market

78

INTERCHANGEABLE SINGLE LAYERS OF THE REACTOR

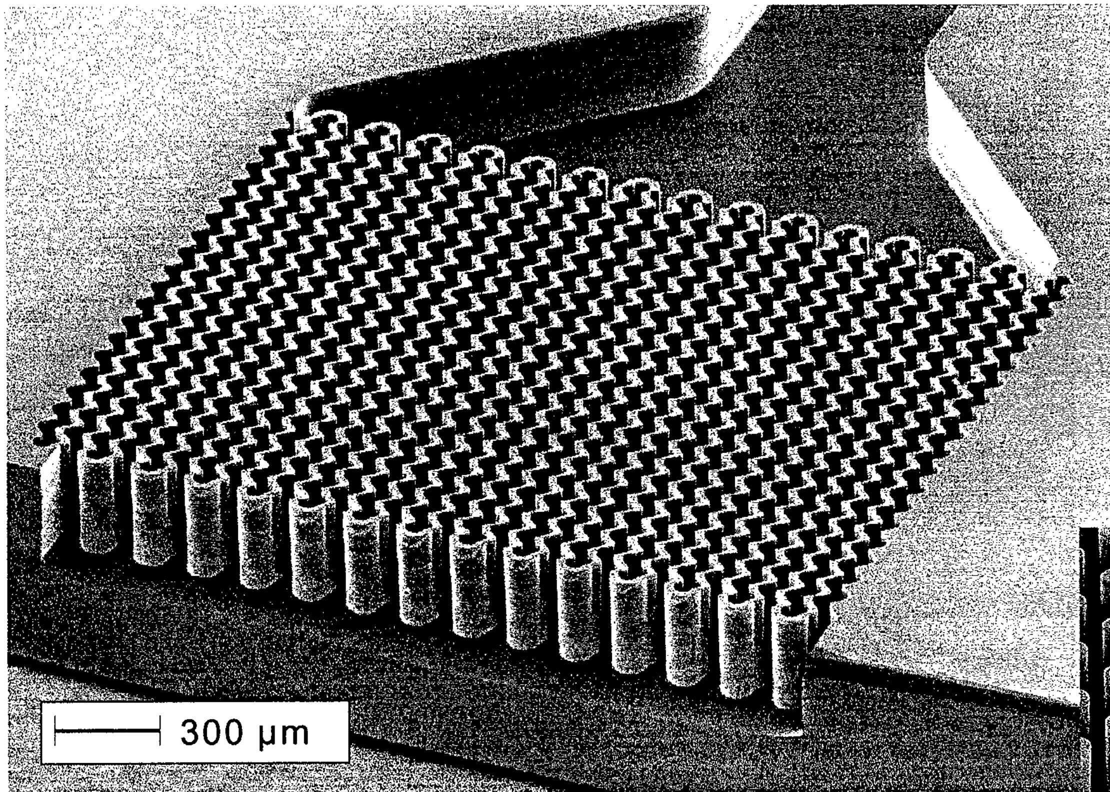


TR E 80423

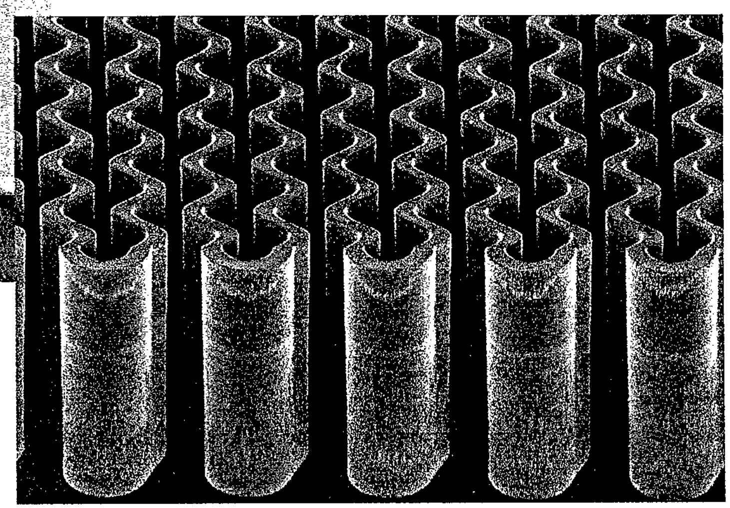
79

MICROMIXER WITH INTERDIGITAL STRUCTURE REALIZED BY ADVANCED SILICON ETCHING

80



- Advanced Silicon Etching
- Silicon, thermally oxidized
- Channel width: 40 µm



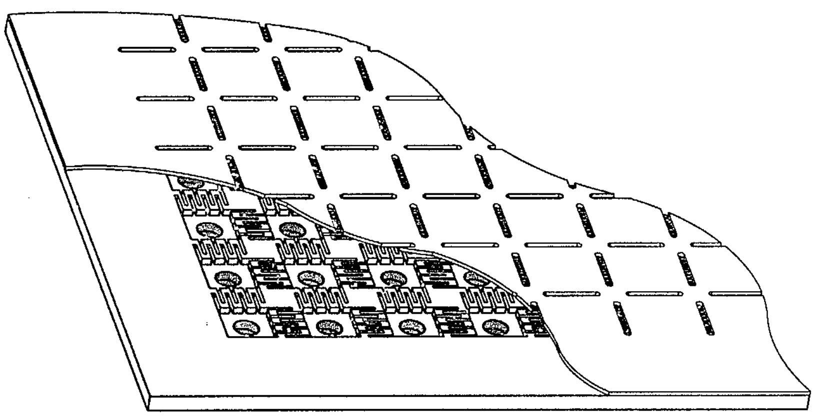
Product development

VH/LA e90008b

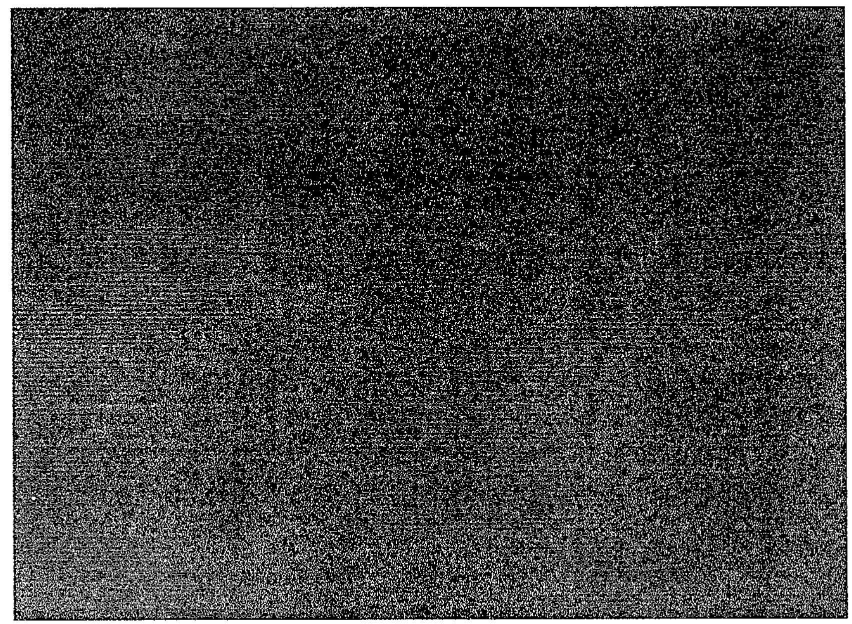
HIGH TROUGH-PUT MICRO MIXER

81

Principle



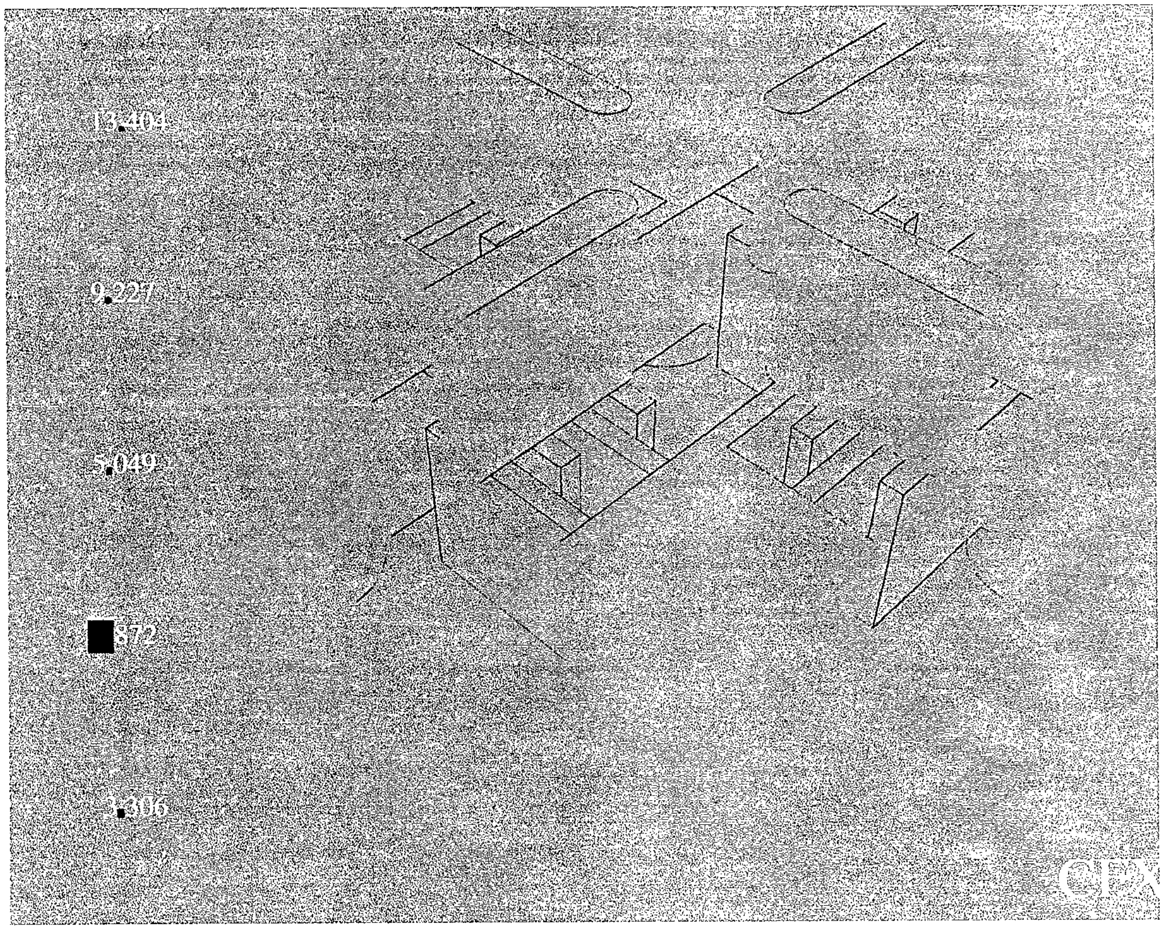
Cr-mask



1560 mixing cells
per micro mixer

E 90342

HIGH THROUGH-PUT MICRO MIXER: FLOW RATE SIMULATION



Pressure distribution (unit: Pa)

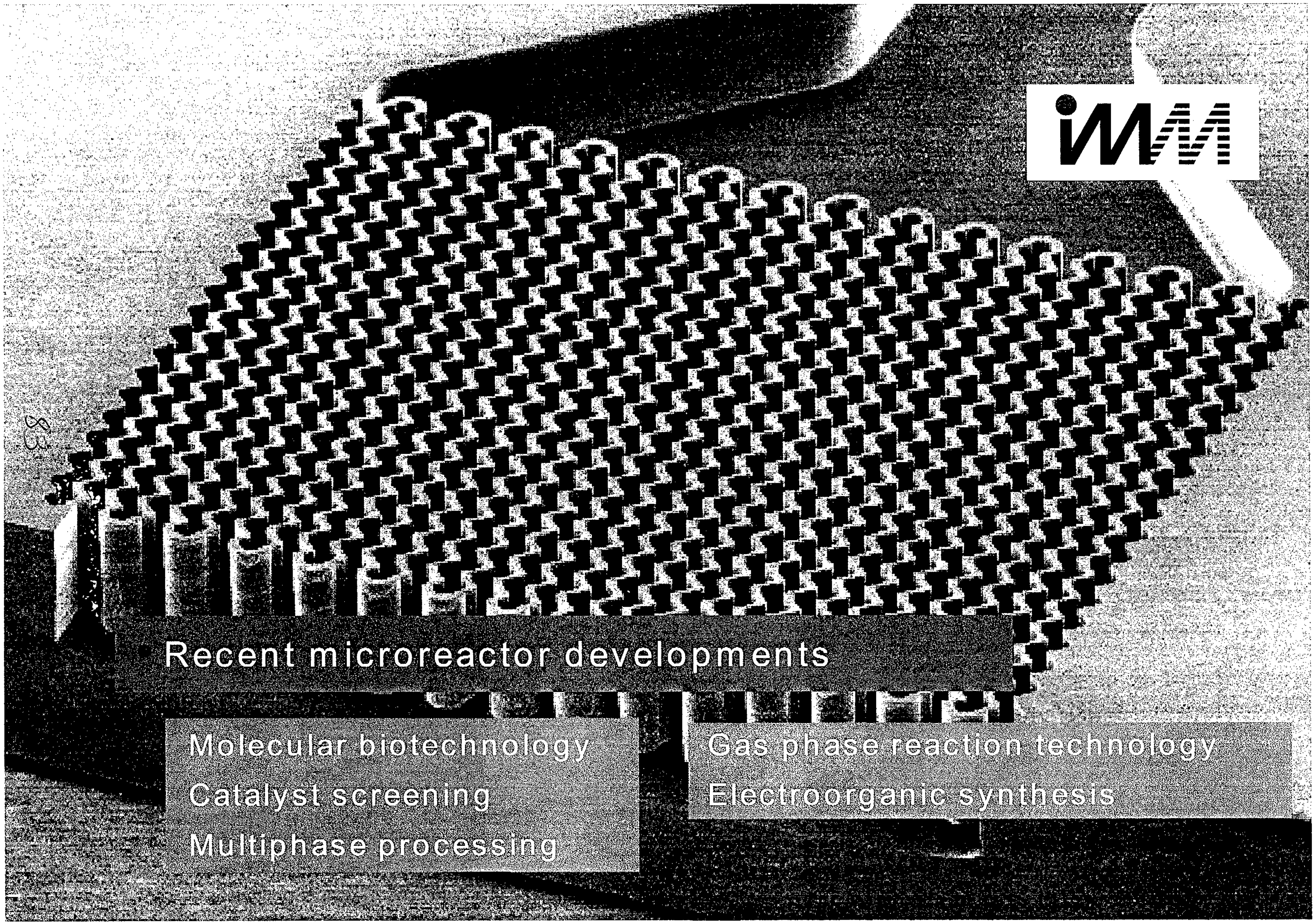
Result
for one mixer
50 mm x 50 mm x 12.5 mm,
2 water-based elements:

Pressure decrease: 0.1 bar

Flow rate: 700 l/h

82

E 90340

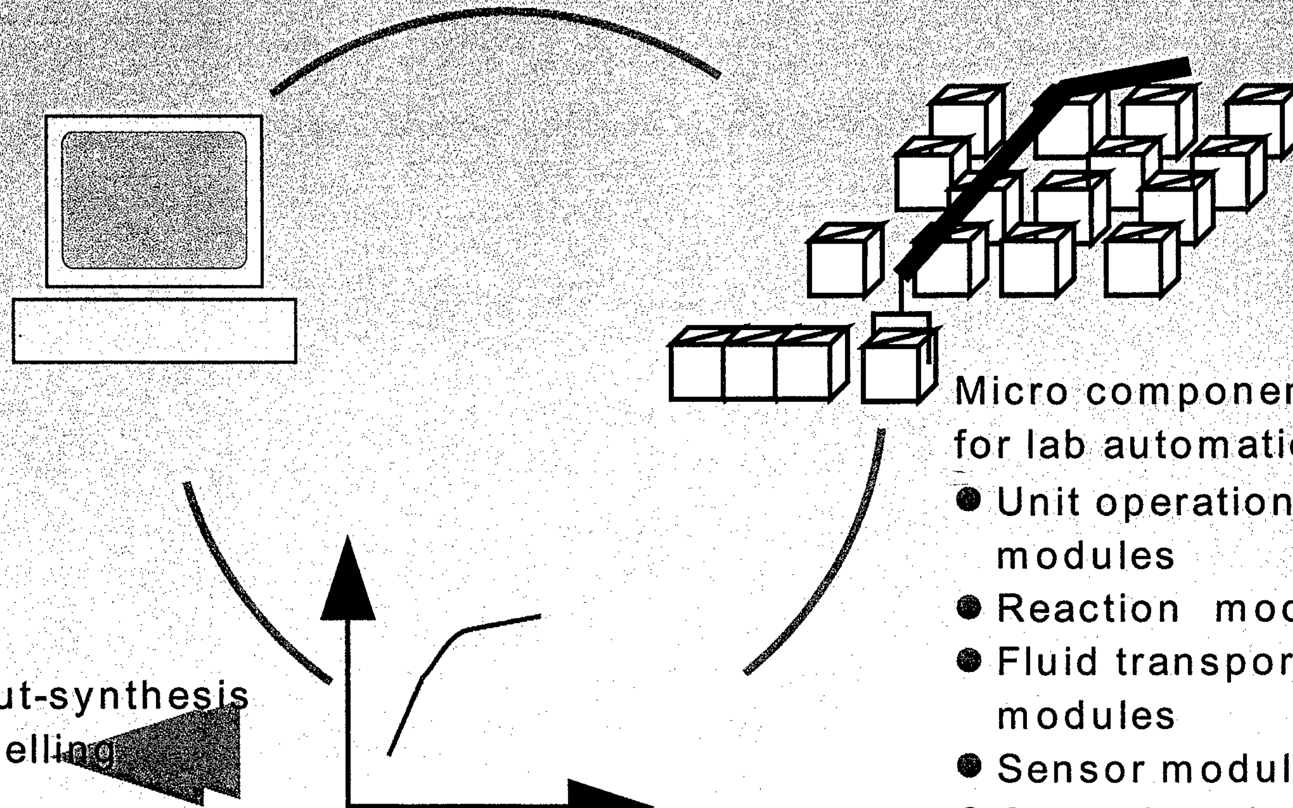

iMM
Recent microreactor developments
Molecular biotechnology
Catalyst screening
Multiphase processing
Gas phase reaction technology
Electroorganic synthesis

83

MODULAR SYSTEMS

IMM

Data for
- highly flexible analyses
- small scale synthesis
- screening and high-throughput-synthesis
- molecular modelling
- ...



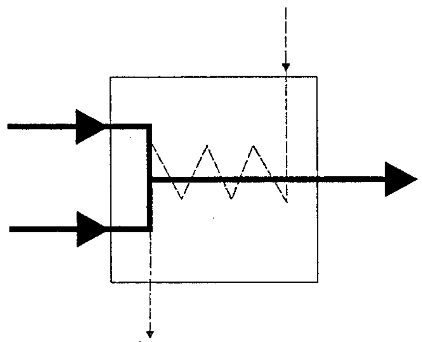
Experimental data

Micro components for lab automation
- Unit operation modules
- Reaction modules
- Fluid transportation modules
- Sensor modules
- Control modules

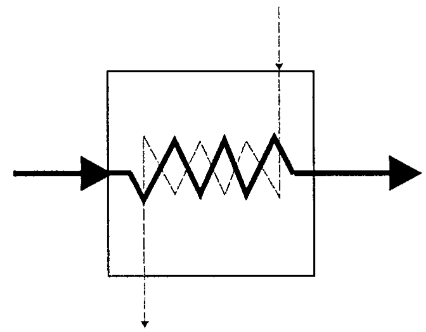
84

E90175

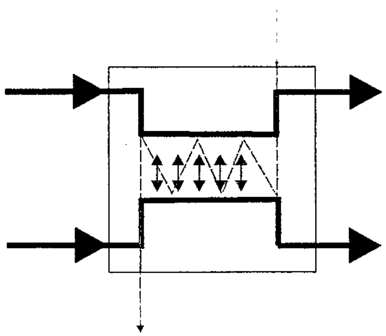
UNIT OPERATION AND REACTION MODULES



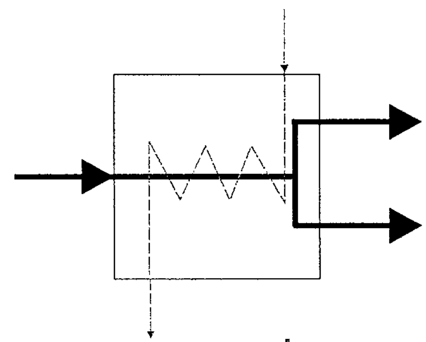
Mixer



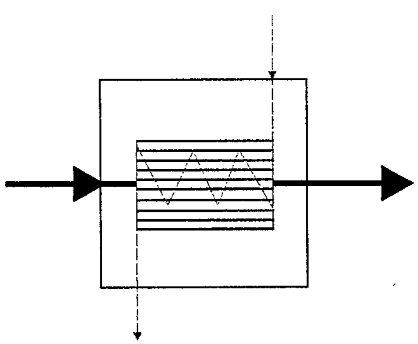
Heat exchanger



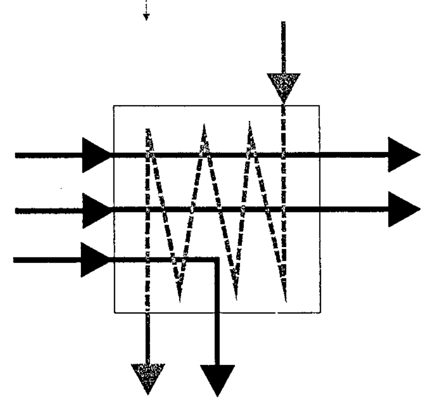
Contactor



Separator



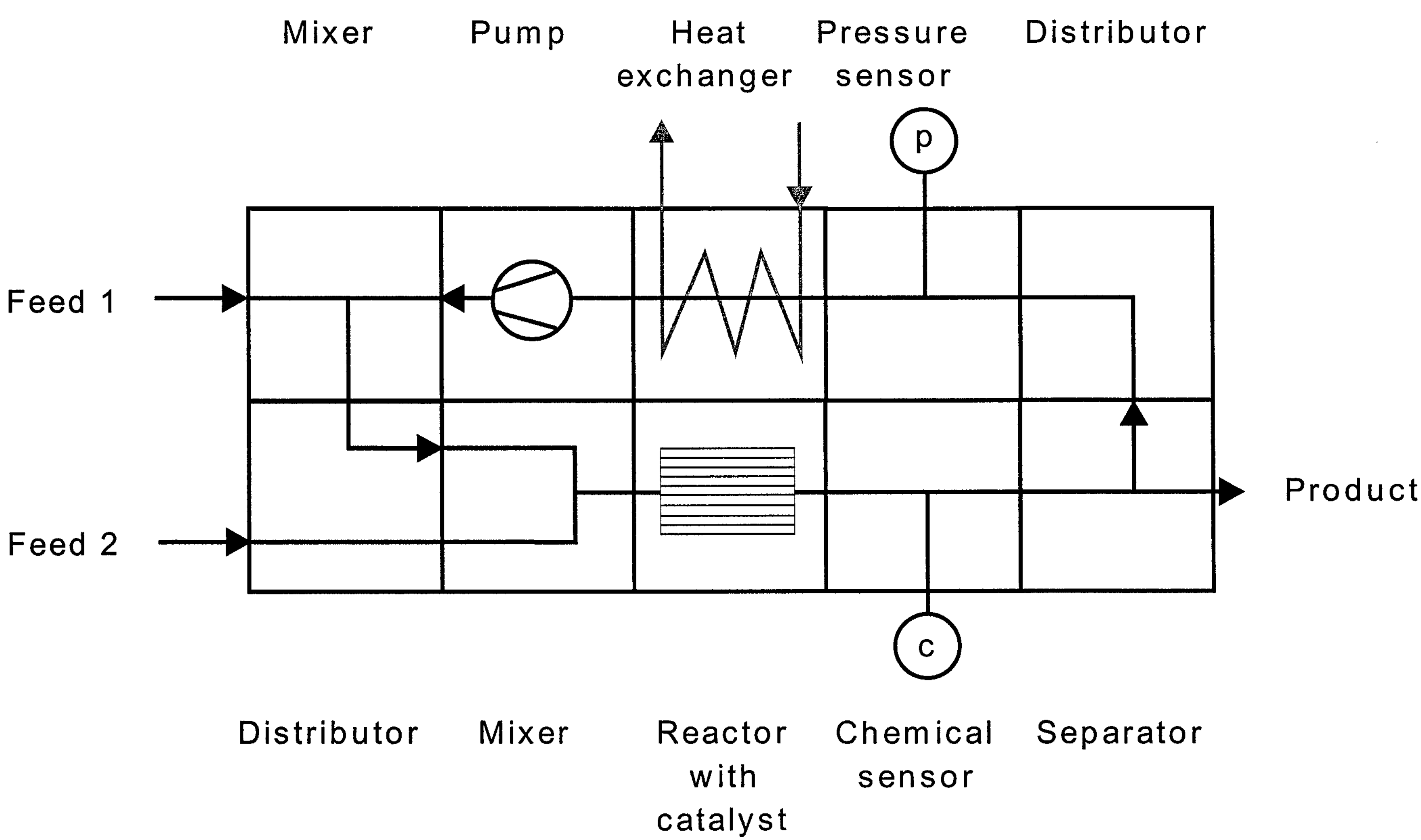
Reactor



Distributor and collector

E90176

MODULAR ASSEMBLY OF MICROREACTOR COMPONENTS



E90174

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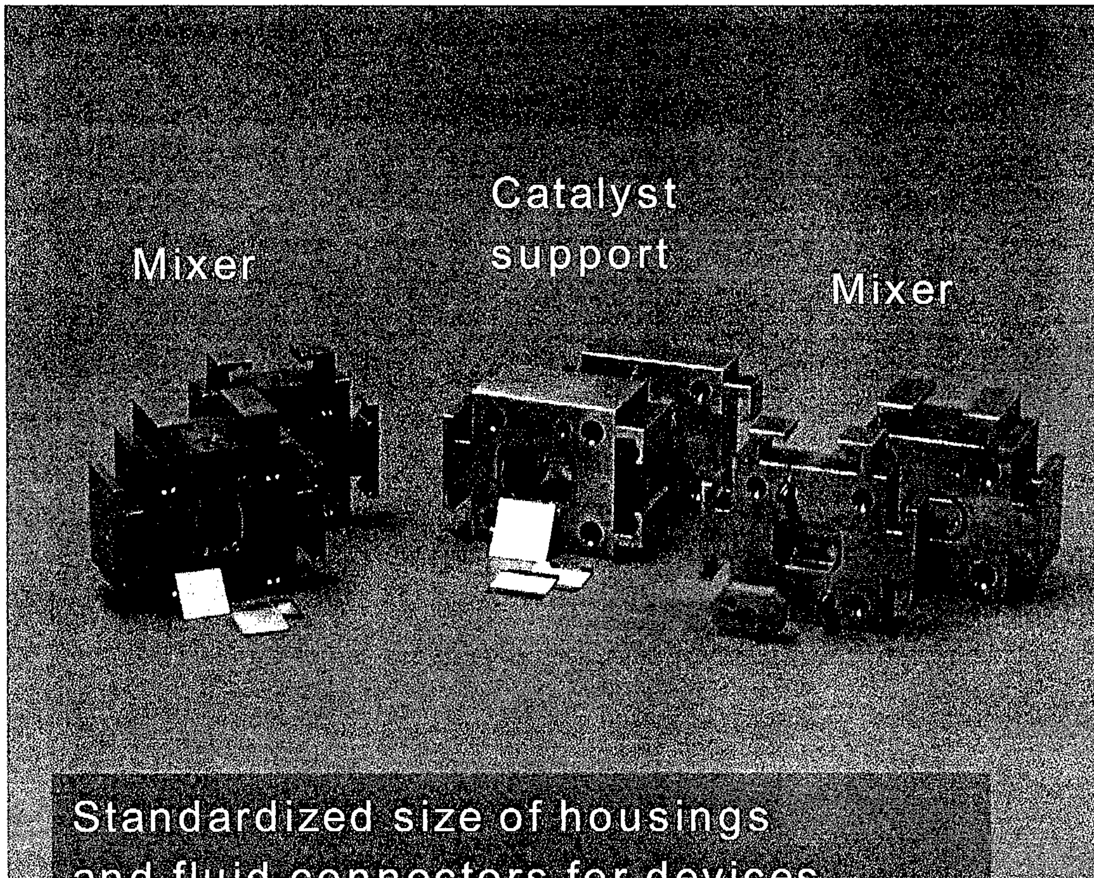
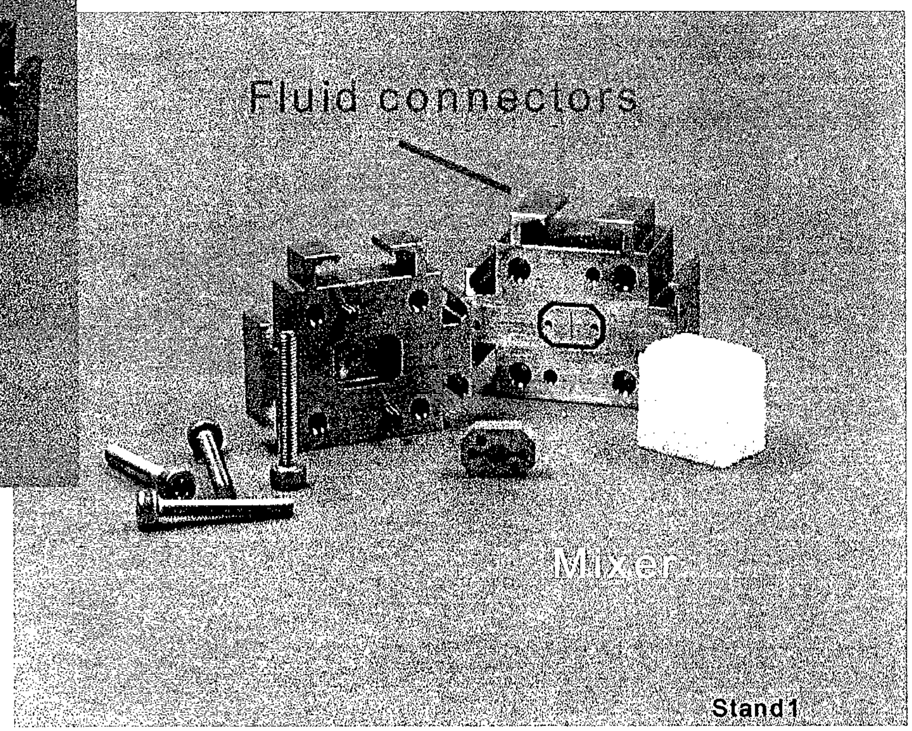
STANDARDIZED HOUSINGS FOR DIFFERENT MICROREACTOR COMPONENTS

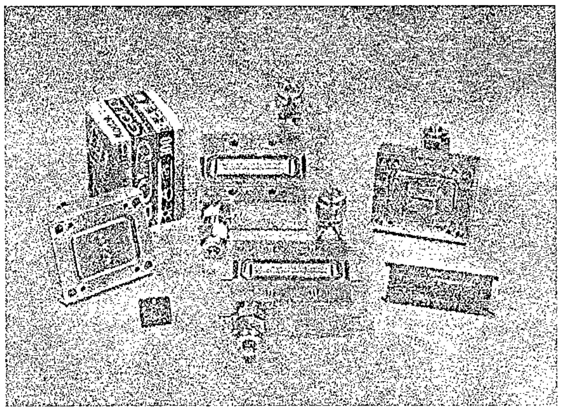


Standardized size of housings
and fluid connectors for devices
performing different unit operations
and reactions

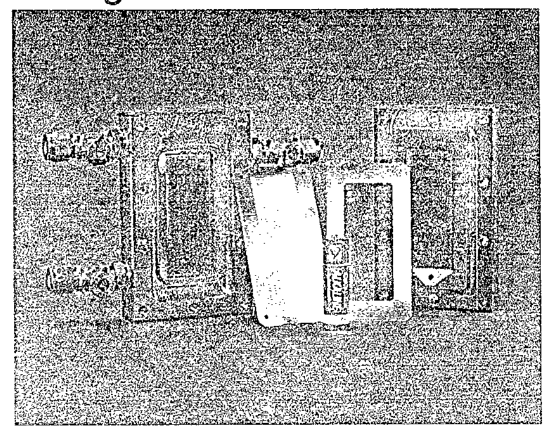


MICROREACTION SYSTEMS (1996-1999): MULTIPHASE REACTORS

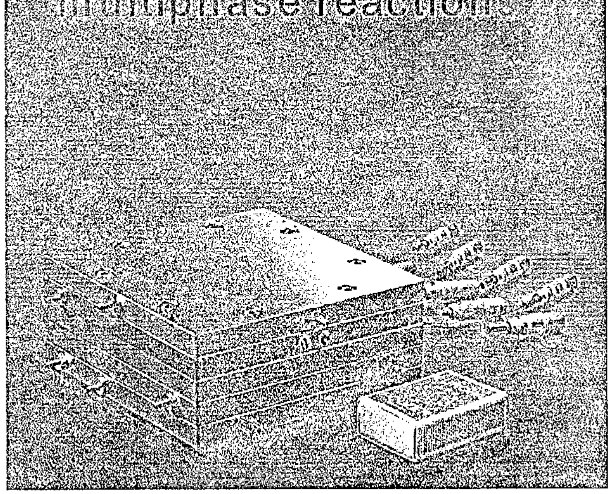
Fluorination of aromatics
Micro bubble column



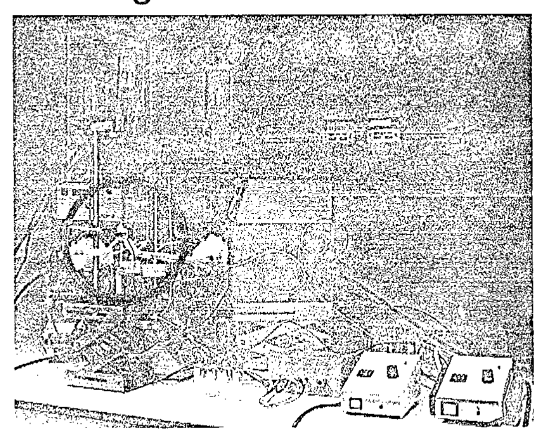
Fluorination of aromatics
Falling film microreactor



Highly exothermal
multiphase reactions

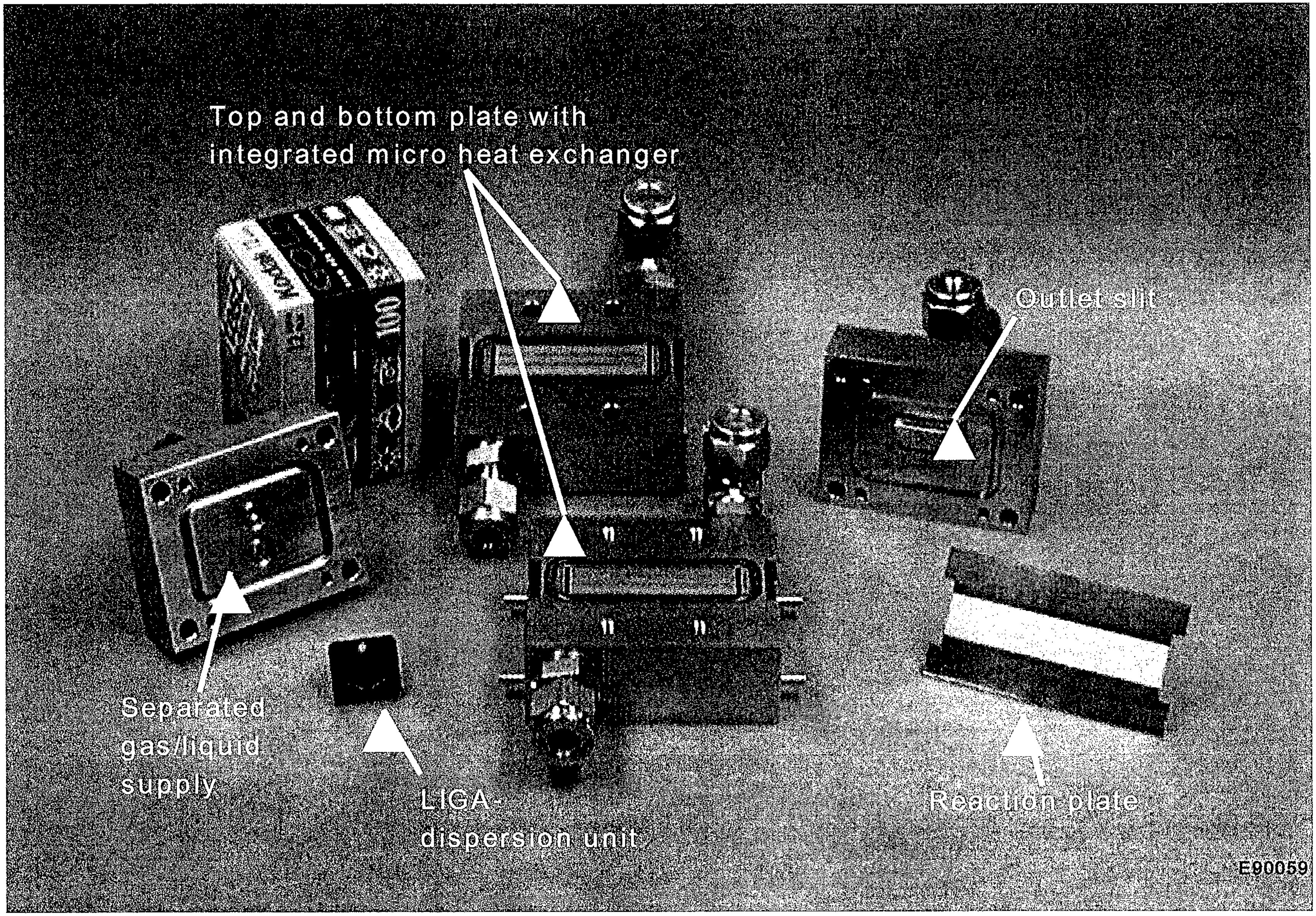


Chemical processing
using micromixers

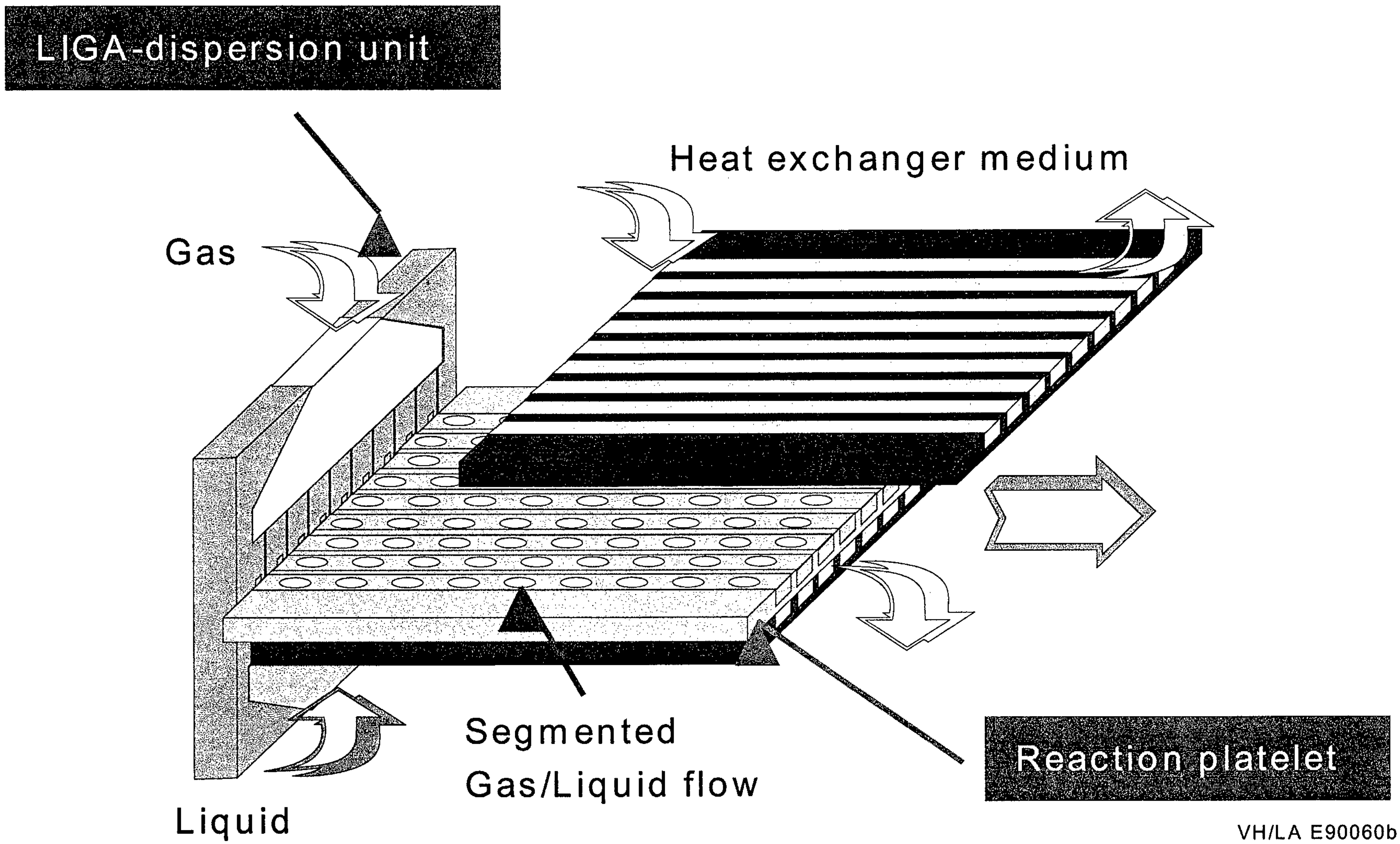


VH/LA E 80480bb

MICRO-BUBBLE COLUMN

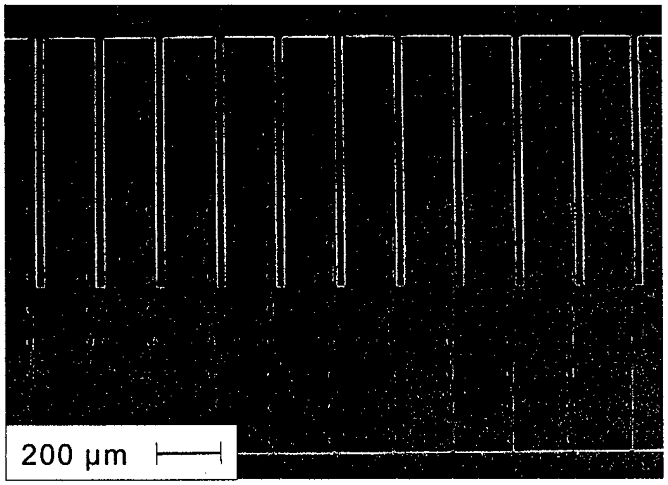


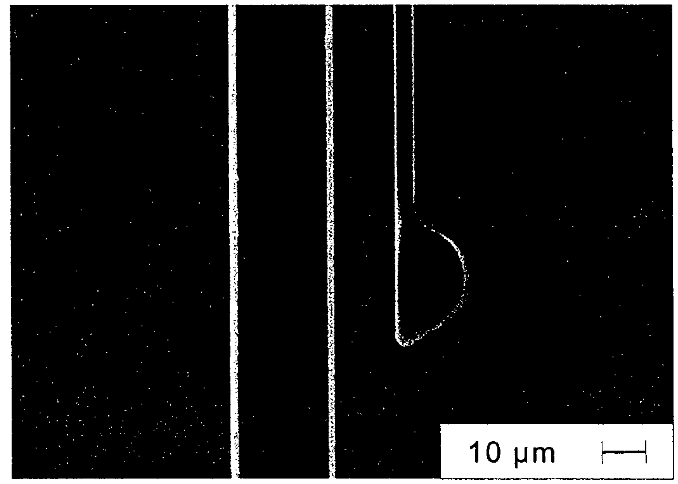
PRINCIPLE DESIGN OF MICRO-BUBBLE COLUMN

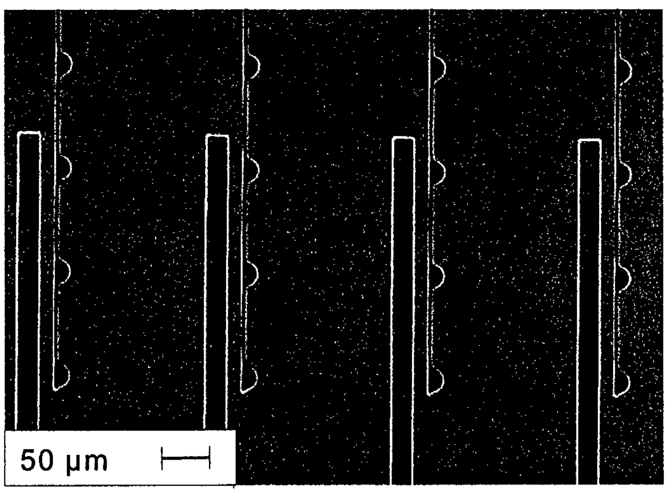


VH/LA E90060b

MICRO-BUBBLE COLUMN: LIGA-DISPERSION UNIT



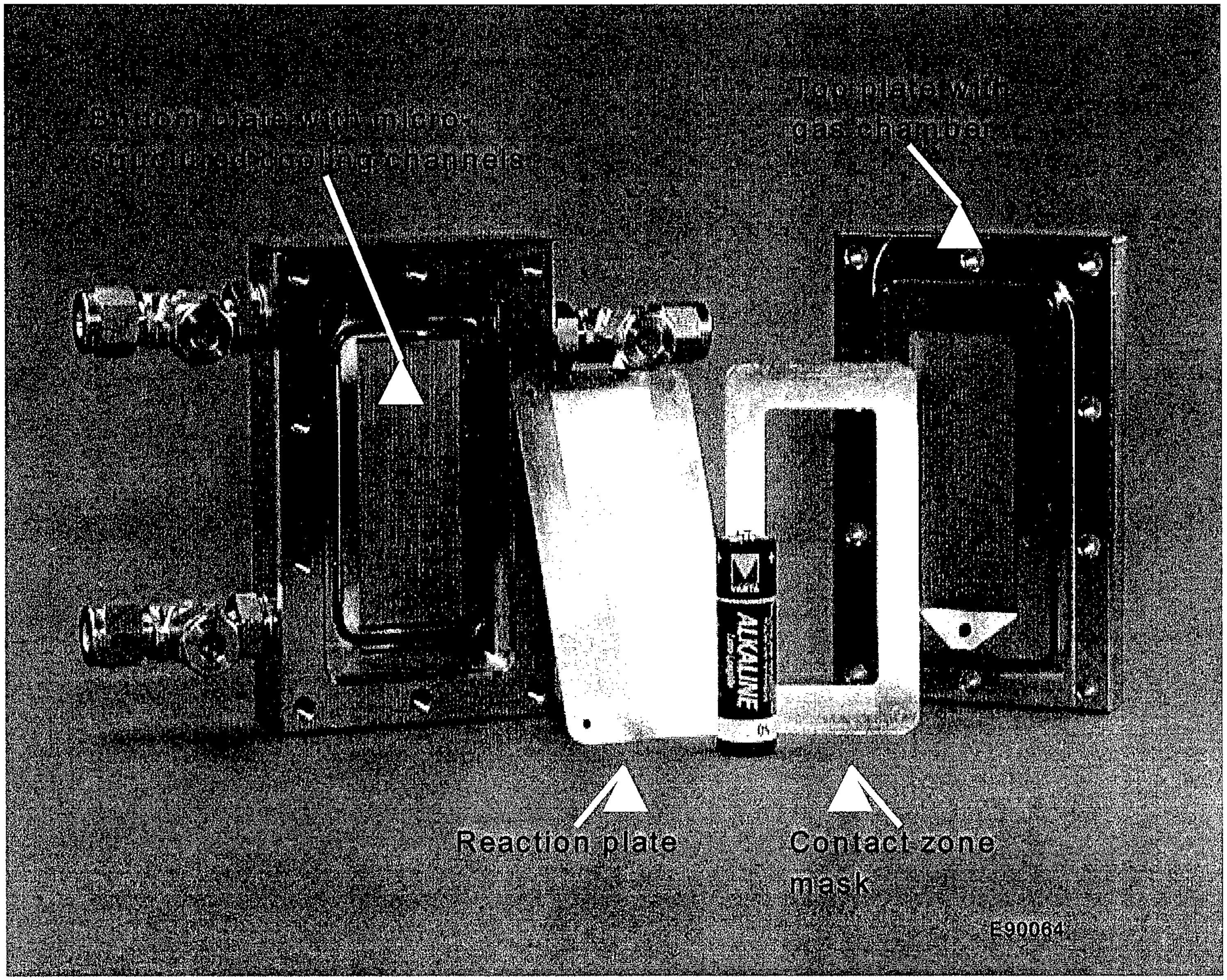




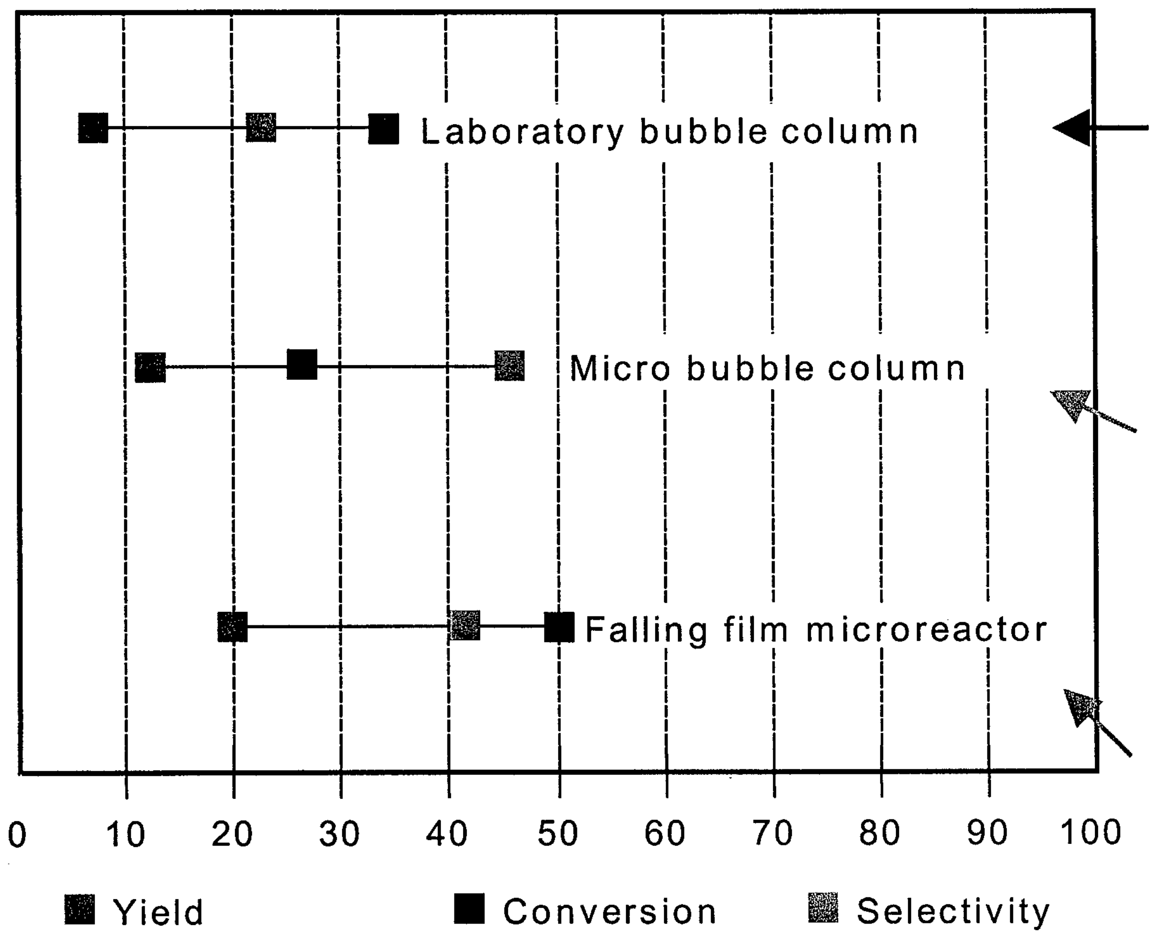
Channel width (gas-side): 3, 5, 10 µm
Channel width (liquid-side): 18, 20 µm
Channel depth: 20 µm

E90062

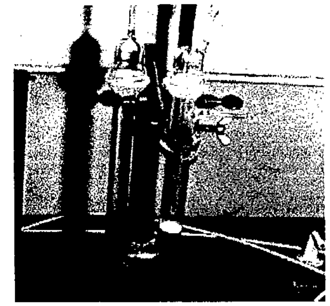
FALLING-FILM MICROREACTOR

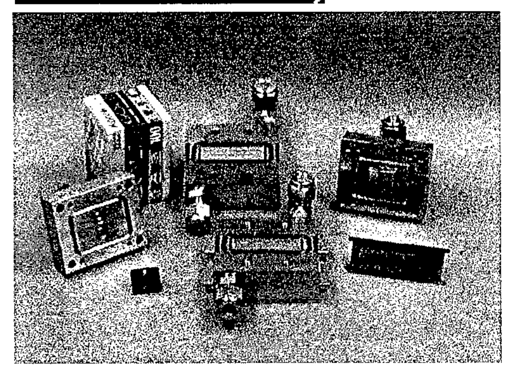


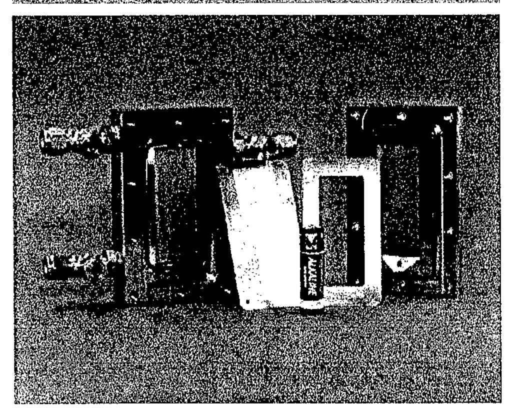
DIRECT FLUORINATION OF TOLUENE DISSOLVED IN ACETONITRILE : HIGHEST YIELDS



Yields based on toluene

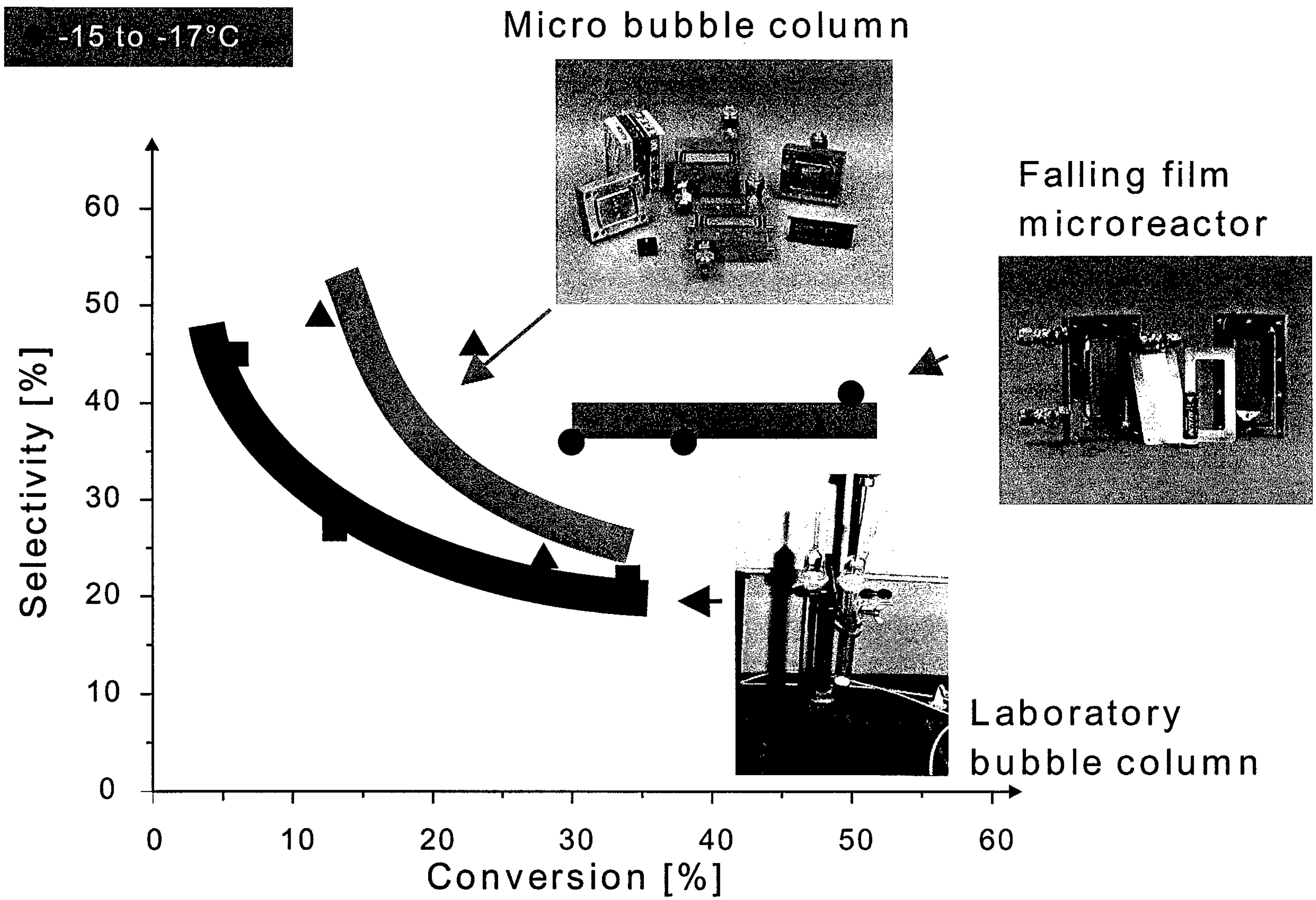






E90199

DIRECT FLUORINATION OF TOLUENE IN ACETONITRILE: SELECTIVITY-CONVERSION GRAPH



E90201

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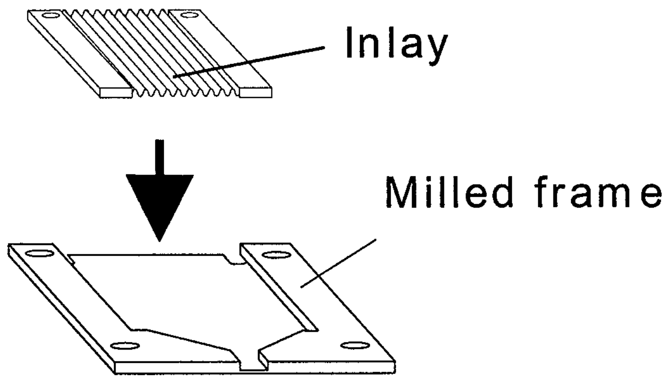
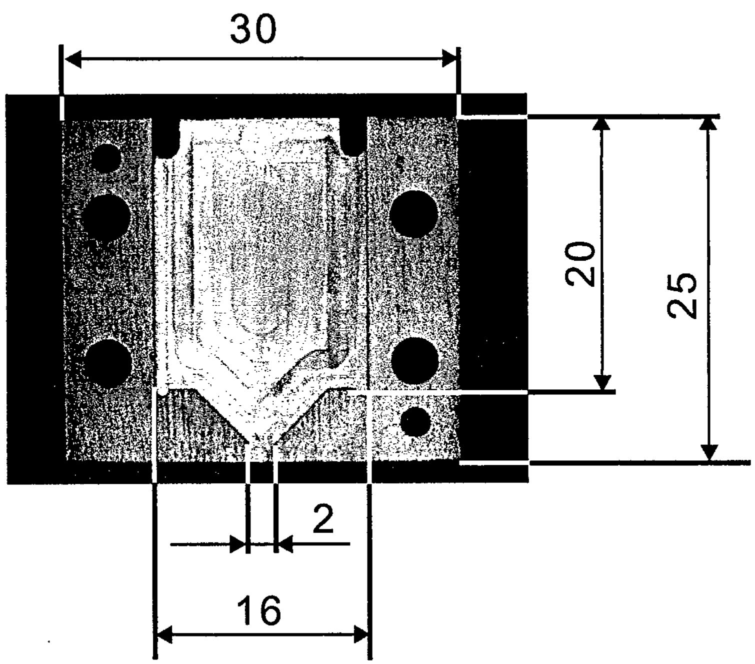
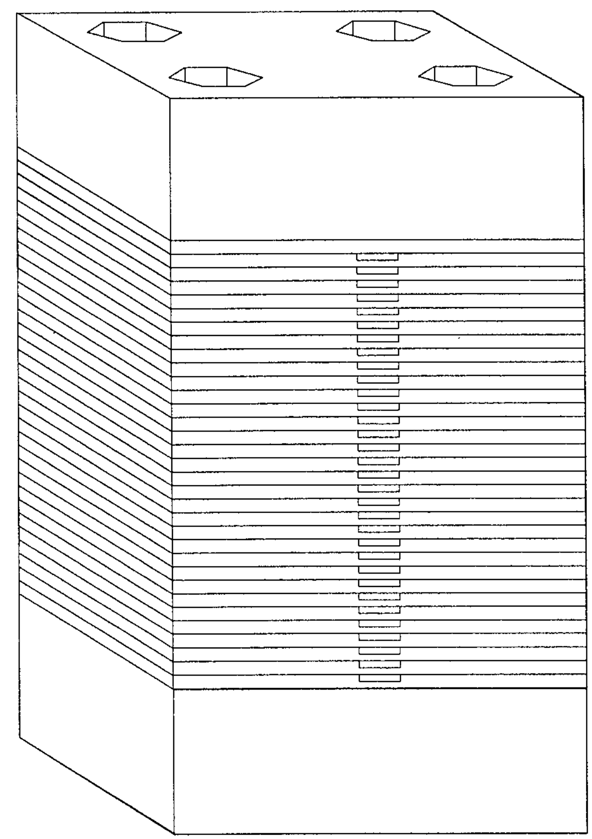
CATALYST SCREENING MODUL



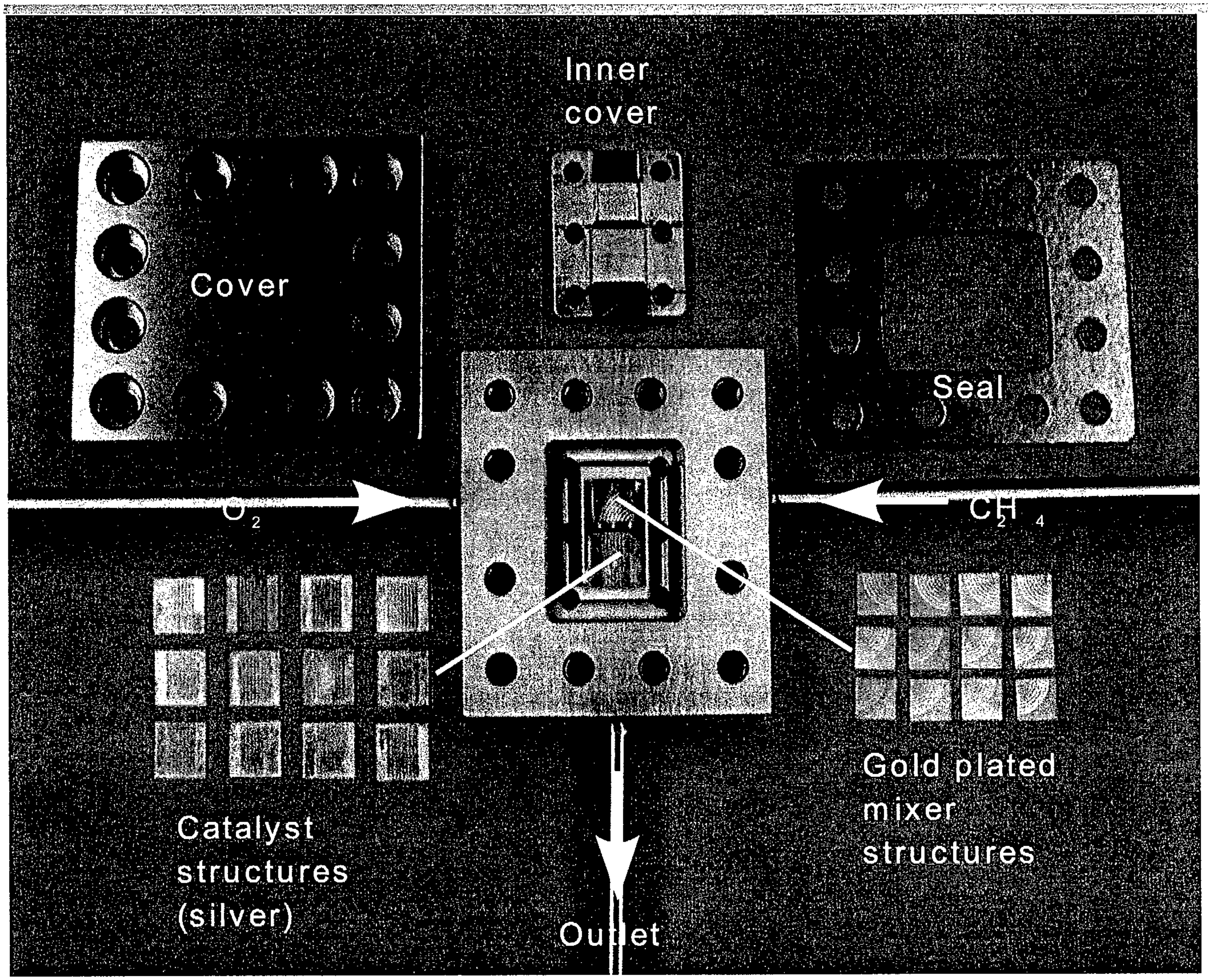




VH/LA E90143b

95

MICROREACTOR FOR ETHYLENE OXIDE SYNTHESIS



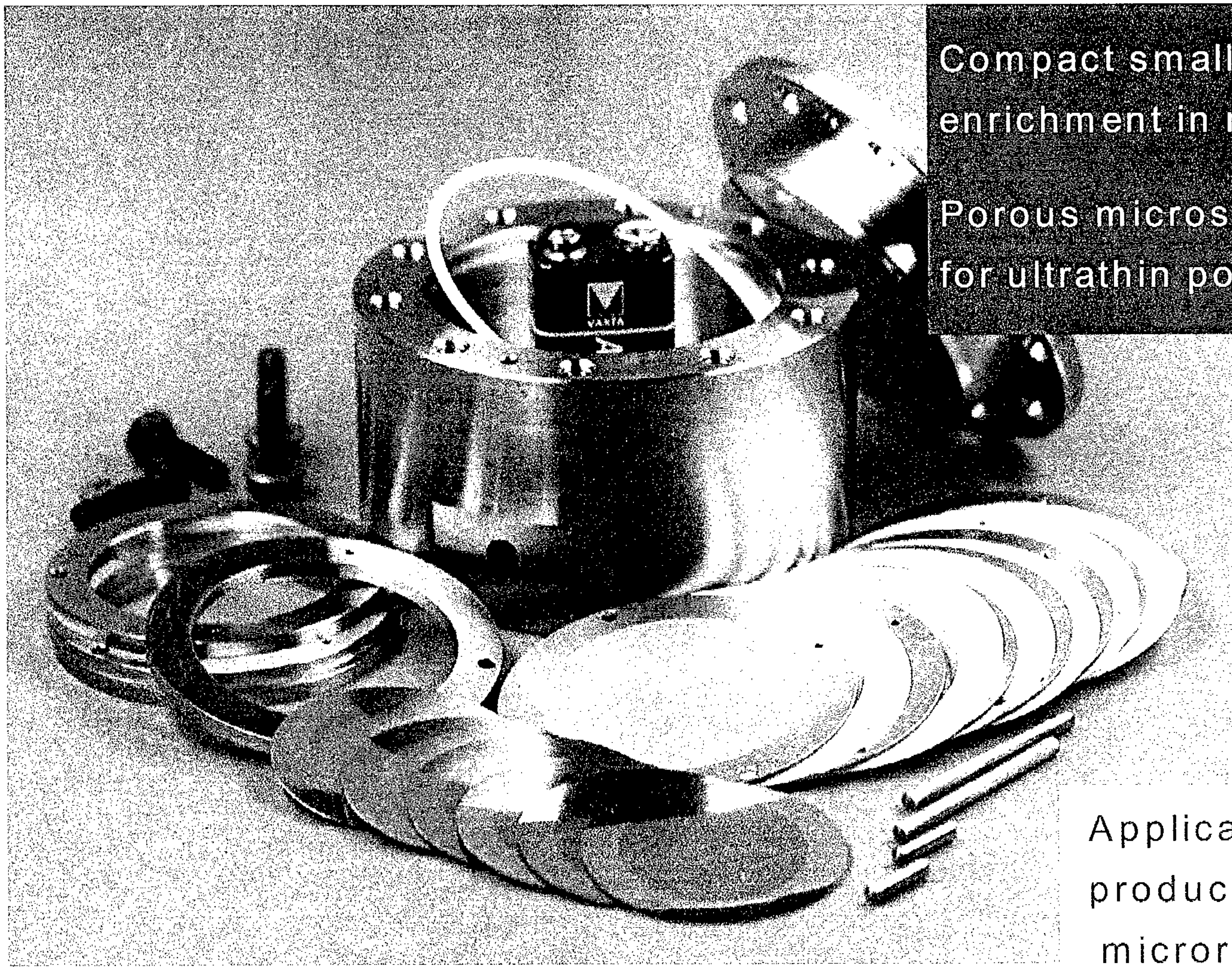
Dismantled microreactor with housing, microstructures, seal and covers

Source: IMM

TR/KG 64709

96

MEMBRANE MODULE FOR GAS SEPARATION



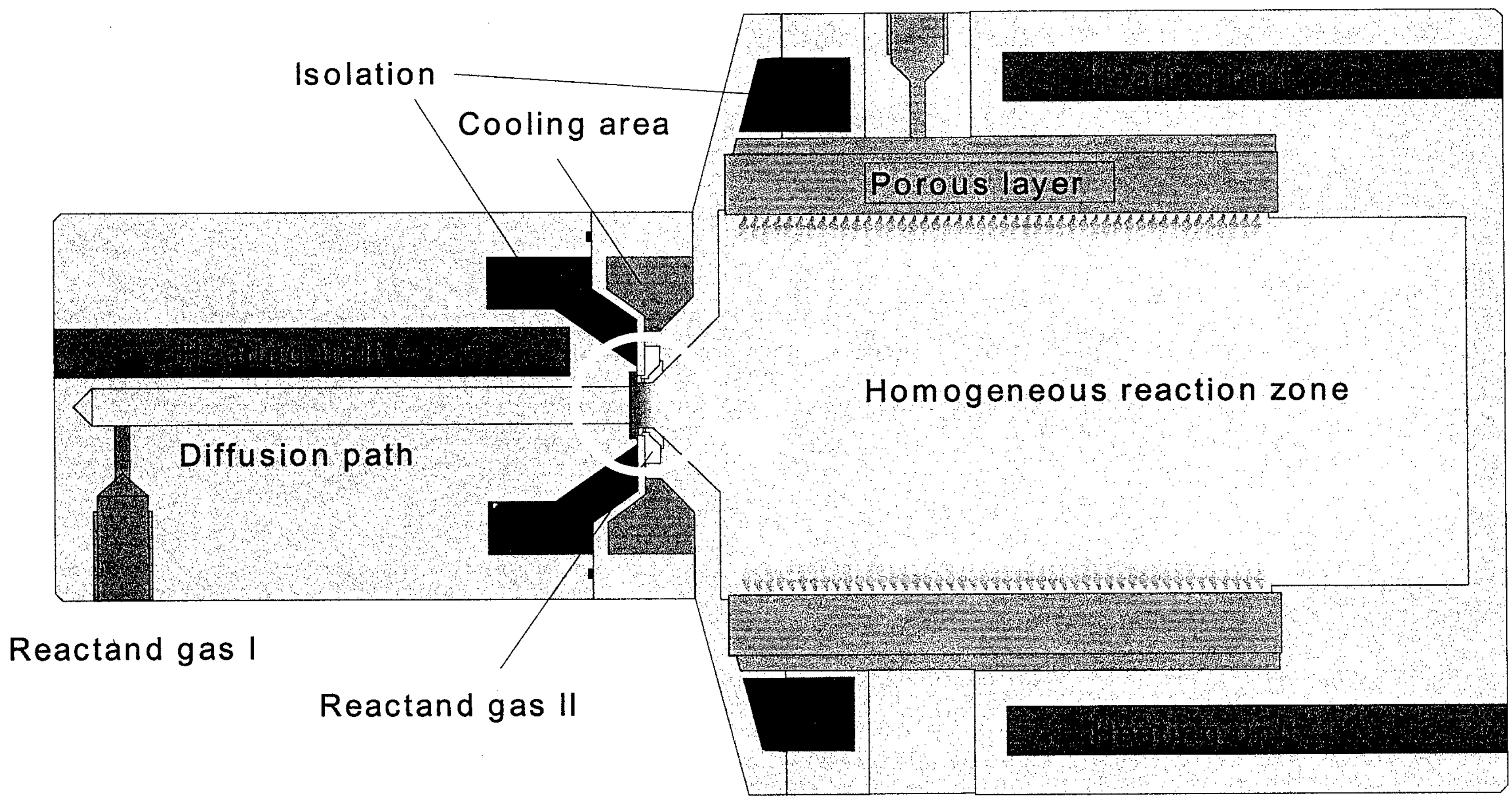
Compact small device for product enrichment in microreactors

Porous microstructured supports for ultrathin polymeric membranes

Application: Separation of products of ethylene oxide microreactor

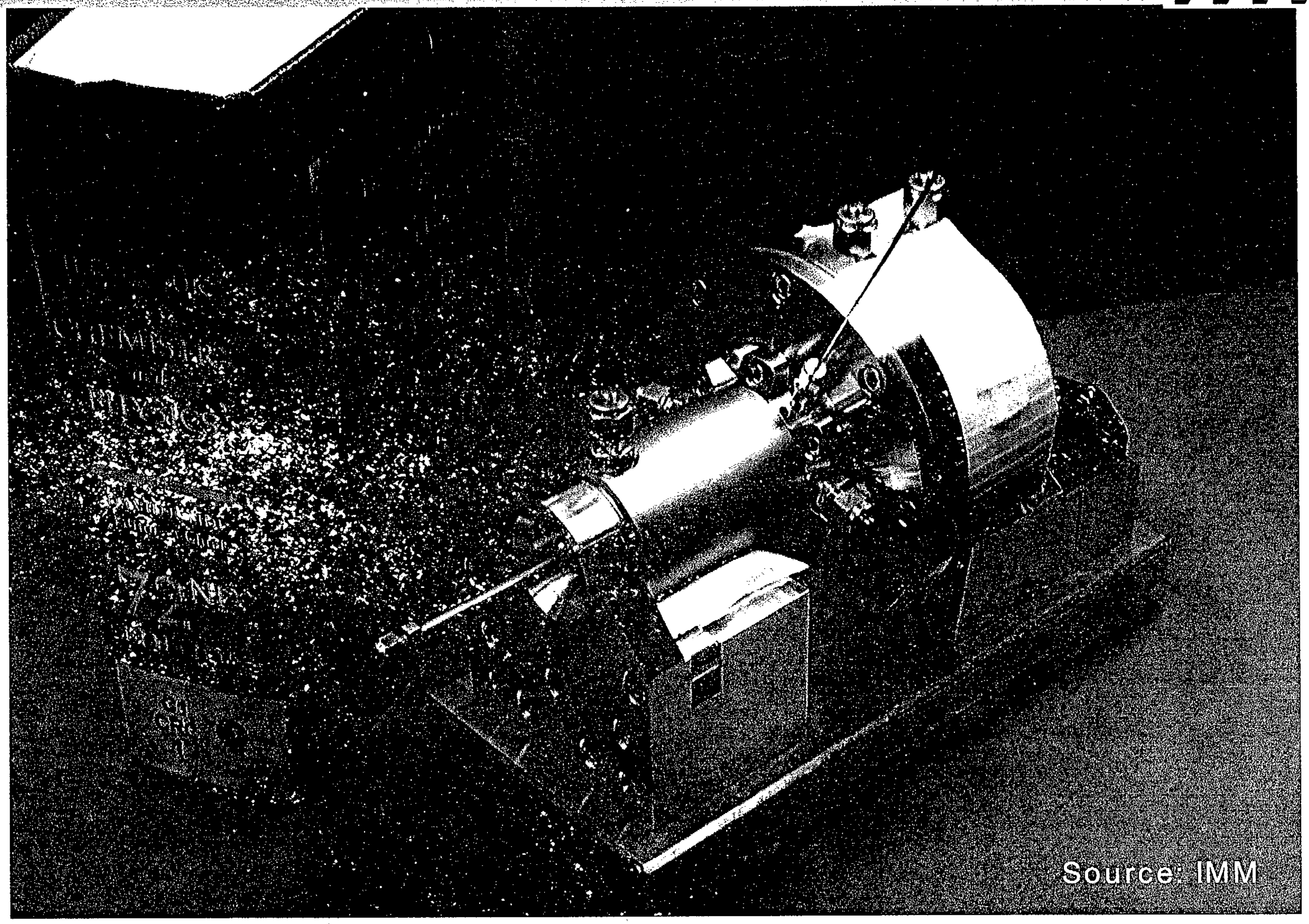
VH/LA membrane

MICROREACTOR FOR PROPENOXIDE SYNTHESIS: SCHEMATIC LAYOUT



TR/OH E 80187

MICROREACTOR FOR PROPENOXIDE SYNTHESIS



TR/DE E 80186

TYPICAL FEATURES OF THE ANDRUSSOW PROCESS

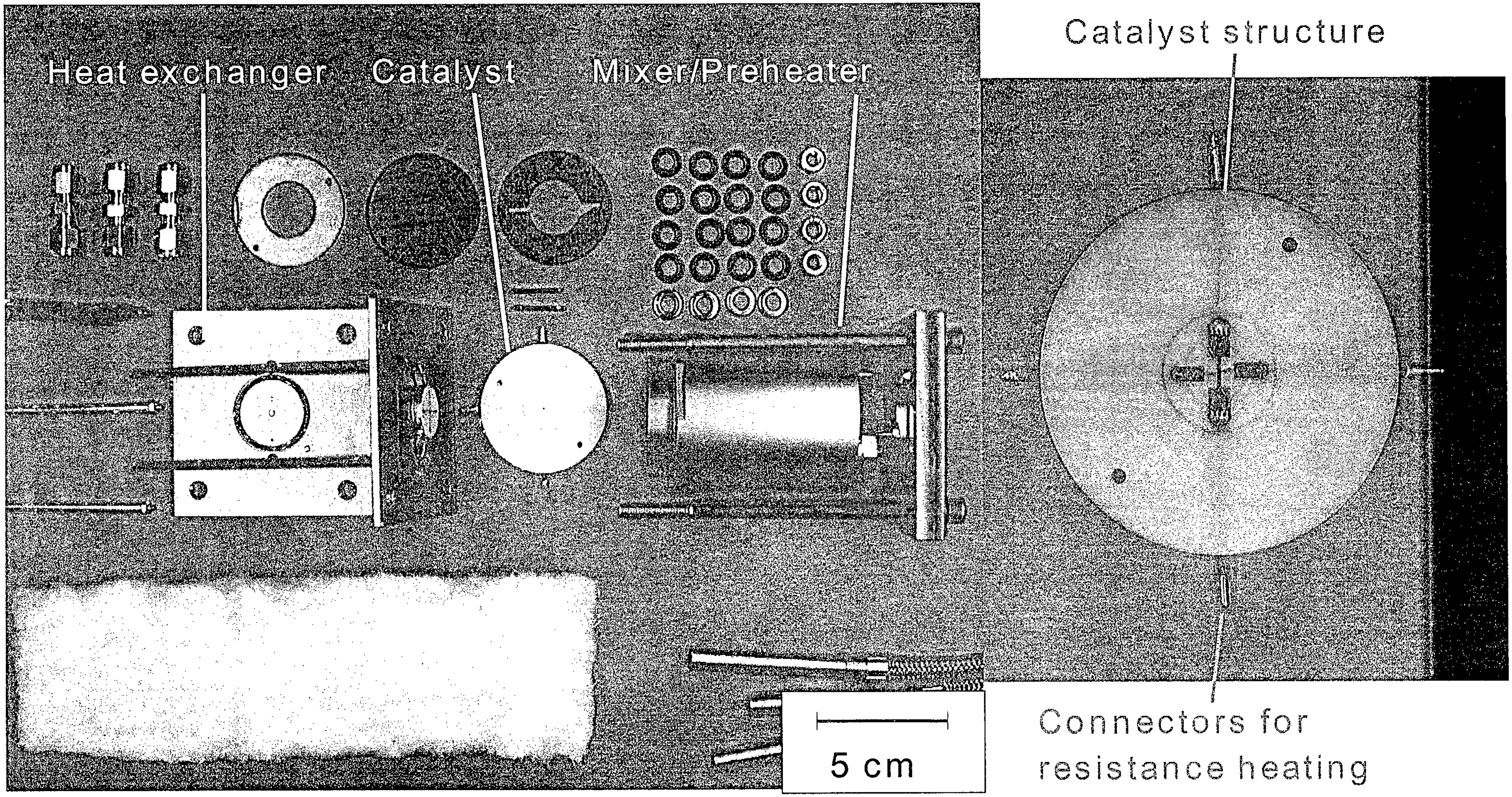
- High reaction temperature (1000 - 1200°C)
- Extremely high velocity of gas streams (3m/s)

$$CH_4 + NH_3 + 3/2\ O_2 \xrightarrow[1000 - 1200°C]{Pt} HCN + 3\ H_2O$$

- Steep temperature gradient (~ 700 - 900°C/s)
- Highly exothermic reaction (- 474 kJ/mol)
- High toxicity of product hydrogen cyanide (lethal dosis: 1 mg /kg body weight)

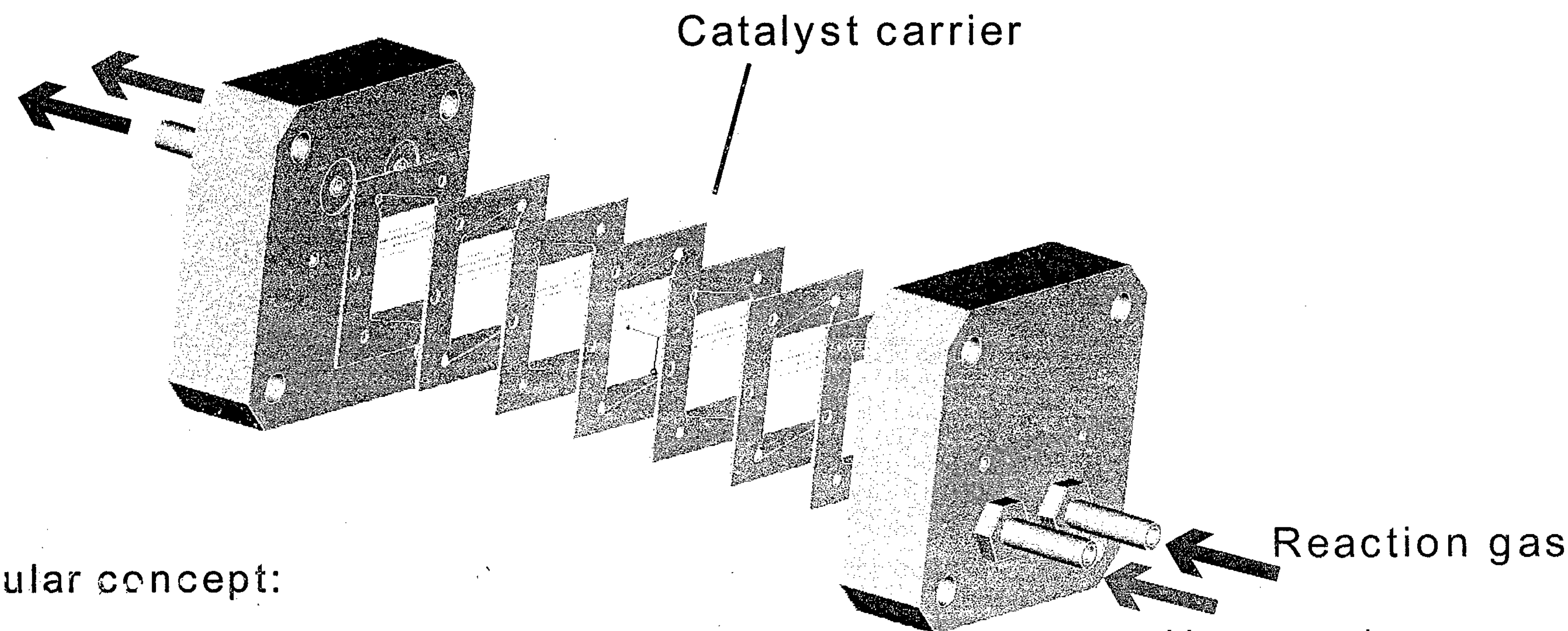
1.4.99 Gol AND8b.cdr

MICROREACTOR FOR THE ANDRUSSOV PROCESS



E90203

MICROREACTOR FOR PERIODIC OPERATION



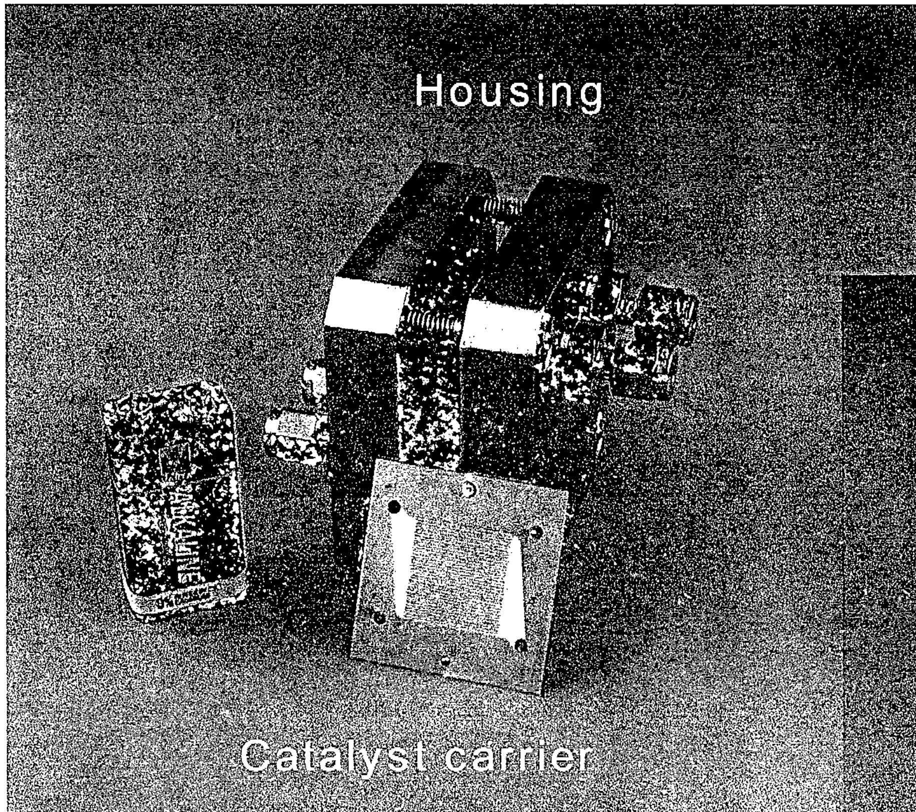
Modular concept:

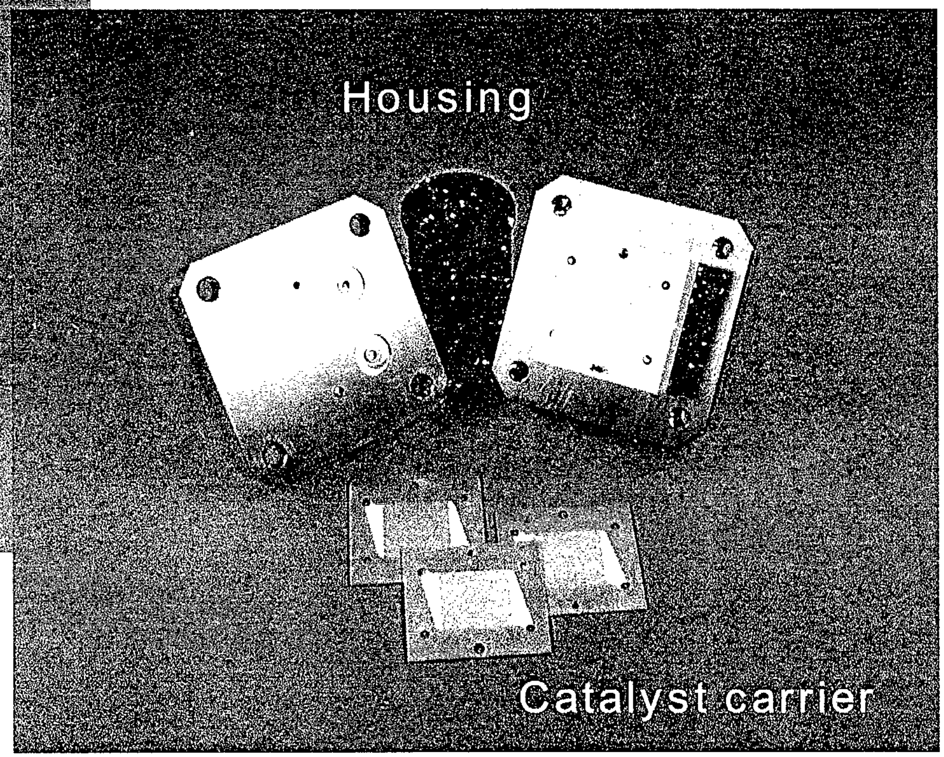
- stainless steel housing
- different materials for catalyst plate: stainless steel, aluminum, titanium
- variable number of catalyst plates

VH/LA E90170

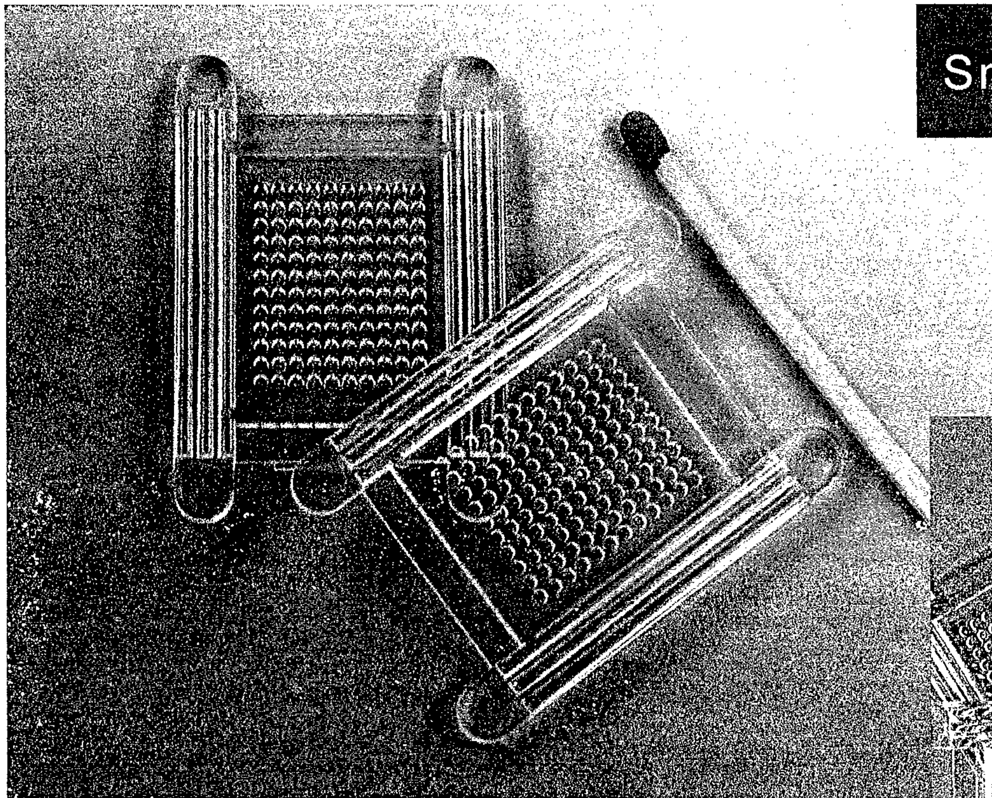
MICROREACTOR FOR PERIODIC OPERATION

Modular concept: variable number of catalyst carriers





NANO TITER PLATES BY INJECTION MOULDING OF POLYCARBONATE ON INSERTED FOILS

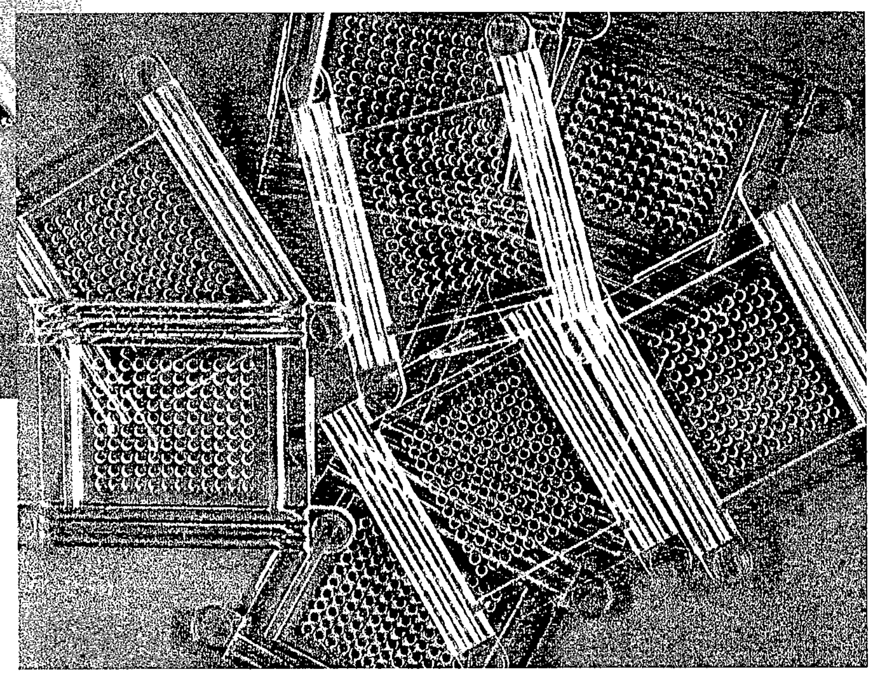


Small-series fabrication

120 wells

Well-to-well spacing: 1.5 mm

Well volume: 0.9 l

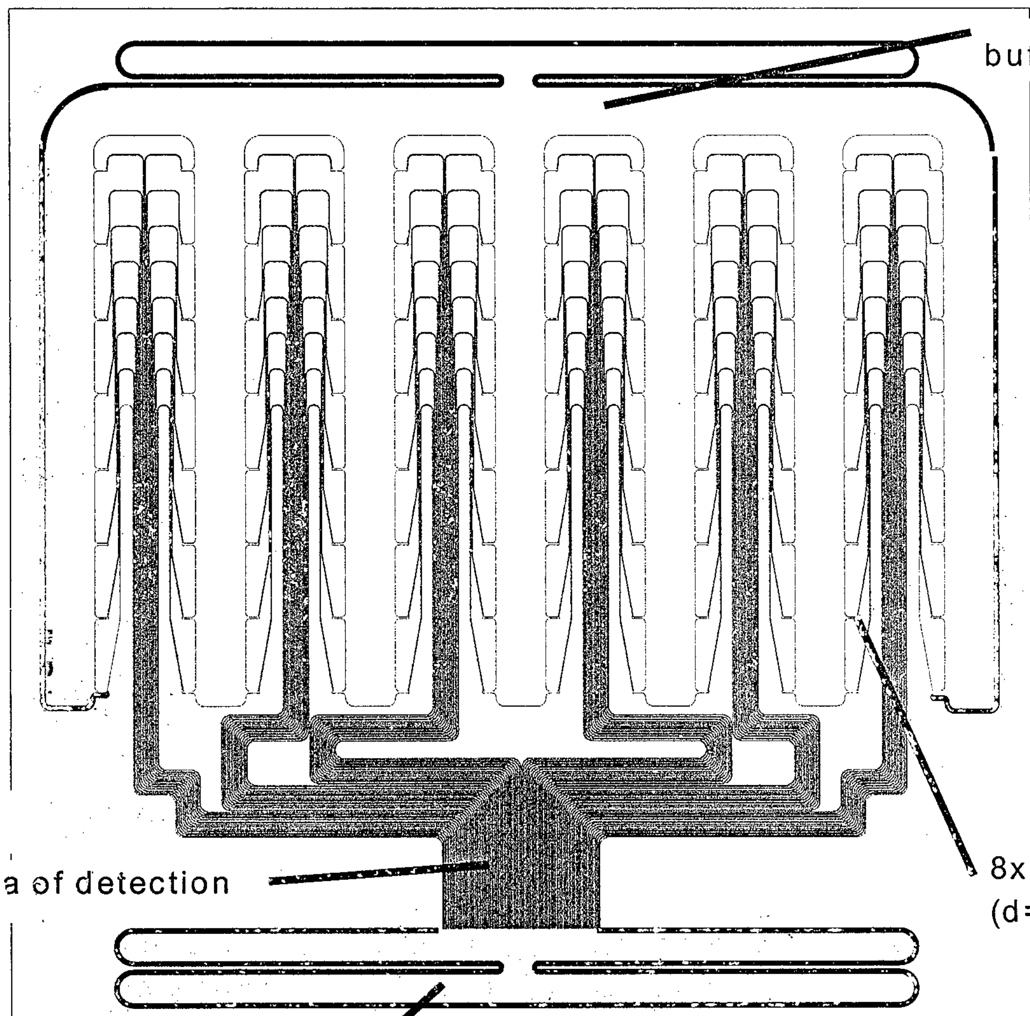


Thin bottom of the wells (120 µm)

MNi Nanotit2

104

DESIGN OF A 96 CHANNEL ELECTROPHORESIS CHIP



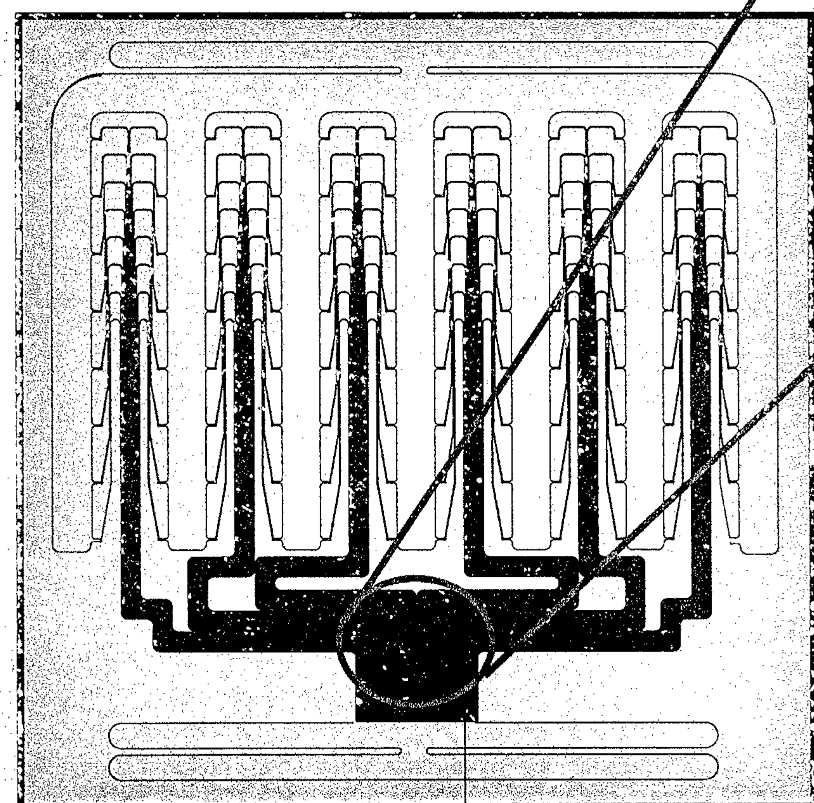
<u>data:</u>

size:	about 60 x 60 mm^2
channels :	50 x 50 µm
separation distance:	67 mm
samples :	96 (about 125 pl)
pitch dimensions :	4,5 mm

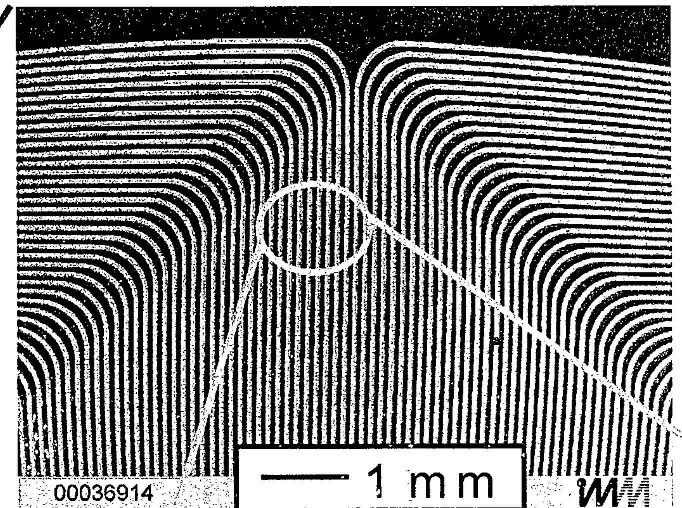
ISo E80505

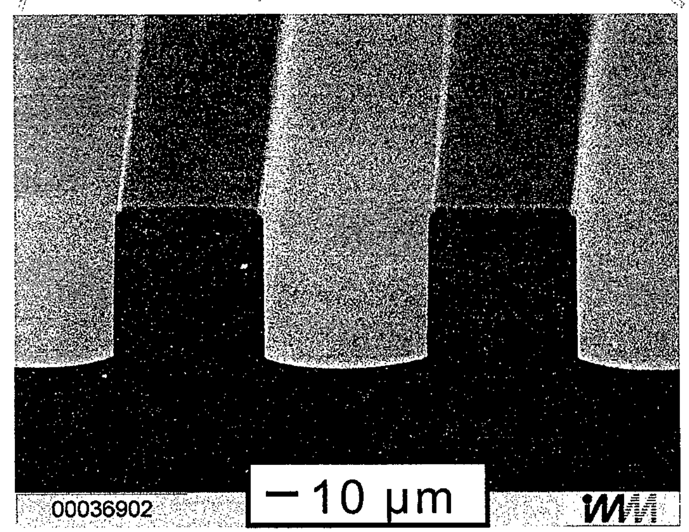
MOLD INSERT: 96 CHANNEL ELECTROPHORESIS CHIP

channels: 50x50 µm
spaces: 50 µm
separation distance: 67 mm



SEM image:





ISo E90133

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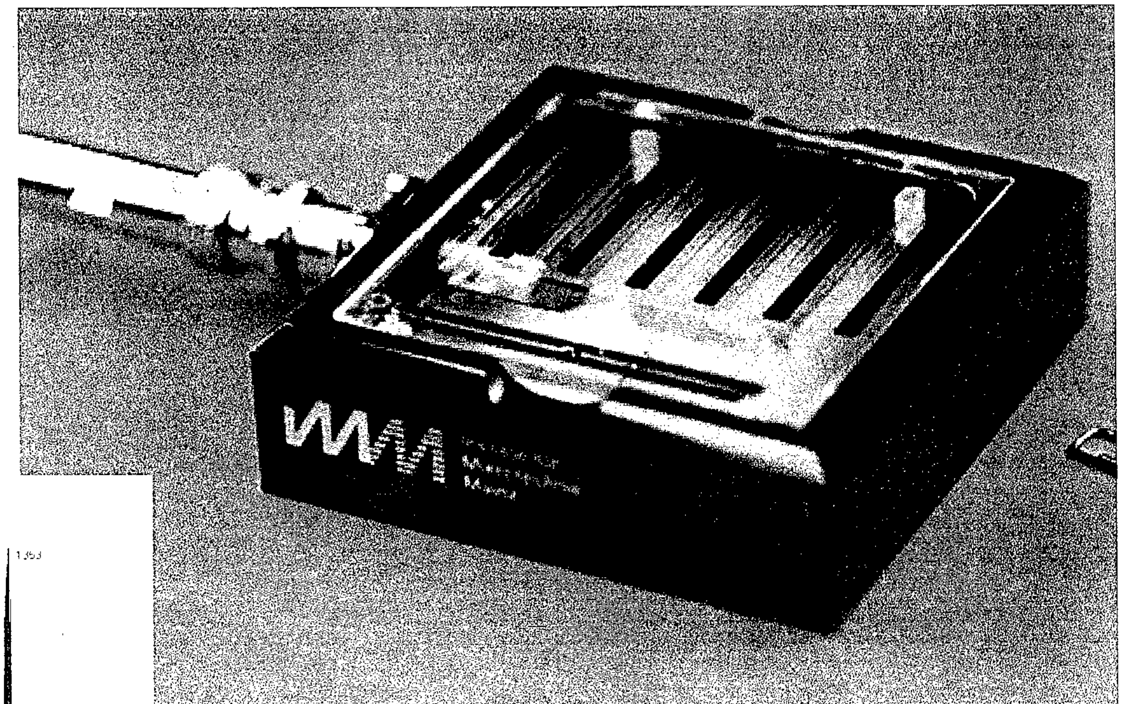
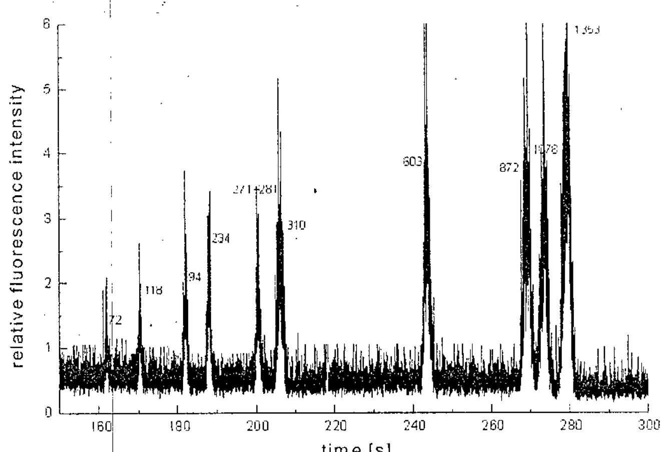
ELECTROPHORETIC SEPARATION OF DNA FRAGMENTS

PMMA chip with interface





source: Uni Heidelberg

sample:	pHi X 174 Hae III dsDNA (10 ng/µl)
gel:	5% Genescan in TTE + 10 nM To-Pro-3-iodid
el. field:	200 V/cm

ISo E90158

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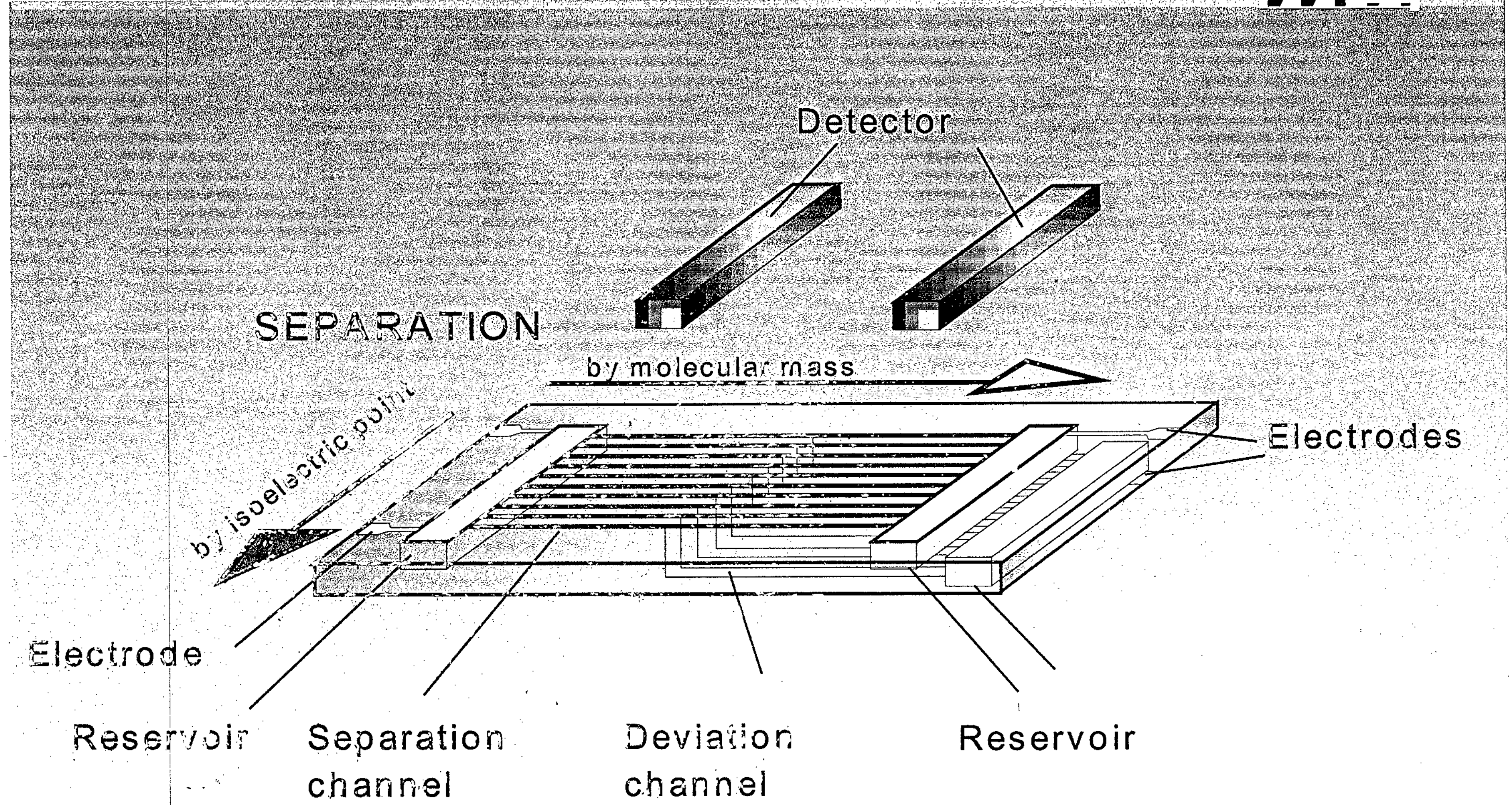
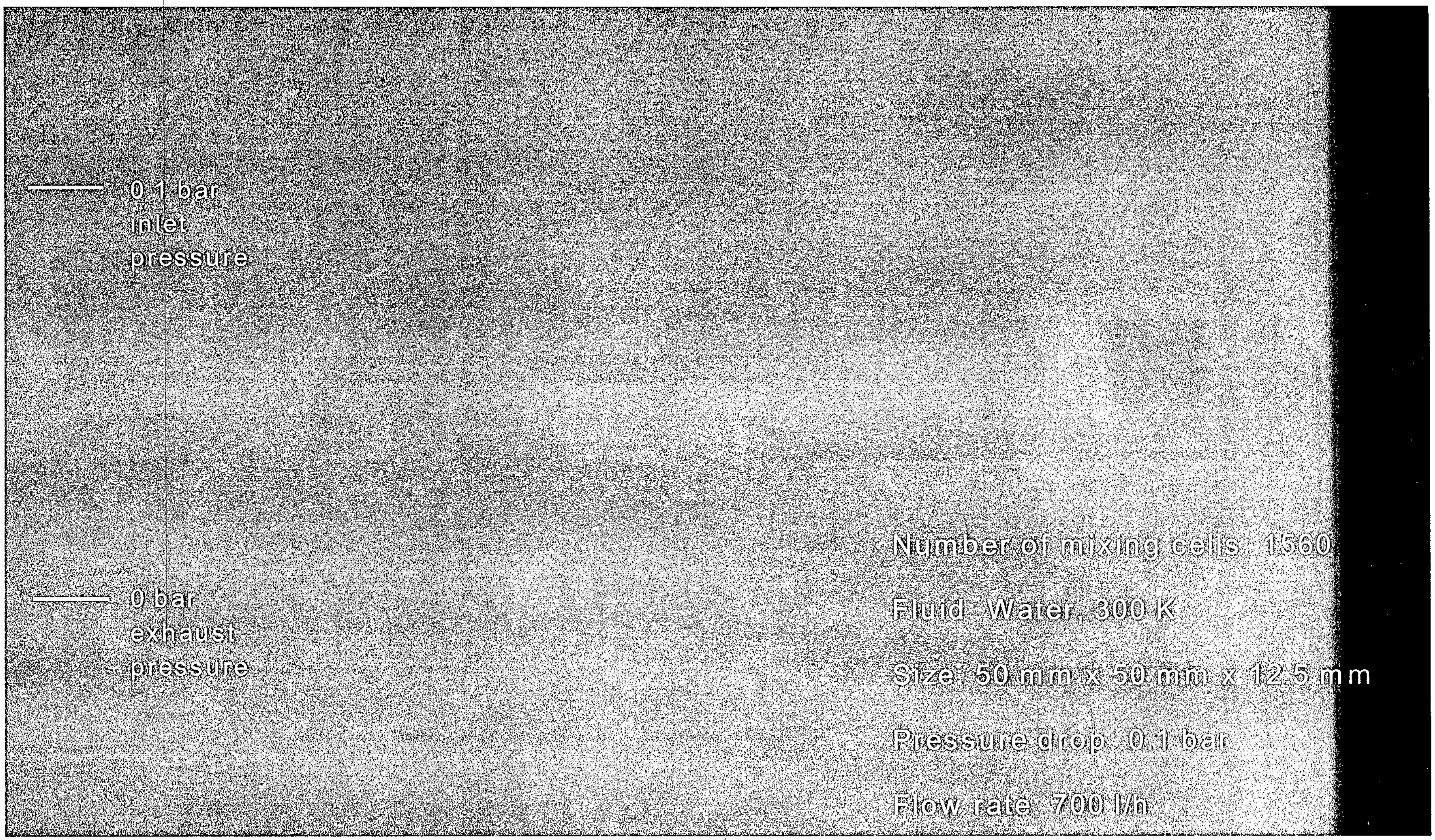
PROTEOMICS 2-D-ELECTROPHORESIS-CHIP



RP 64982

HIGH THROUGHPUT MICRO MIXER: FLOW SIMULATION



E 90340

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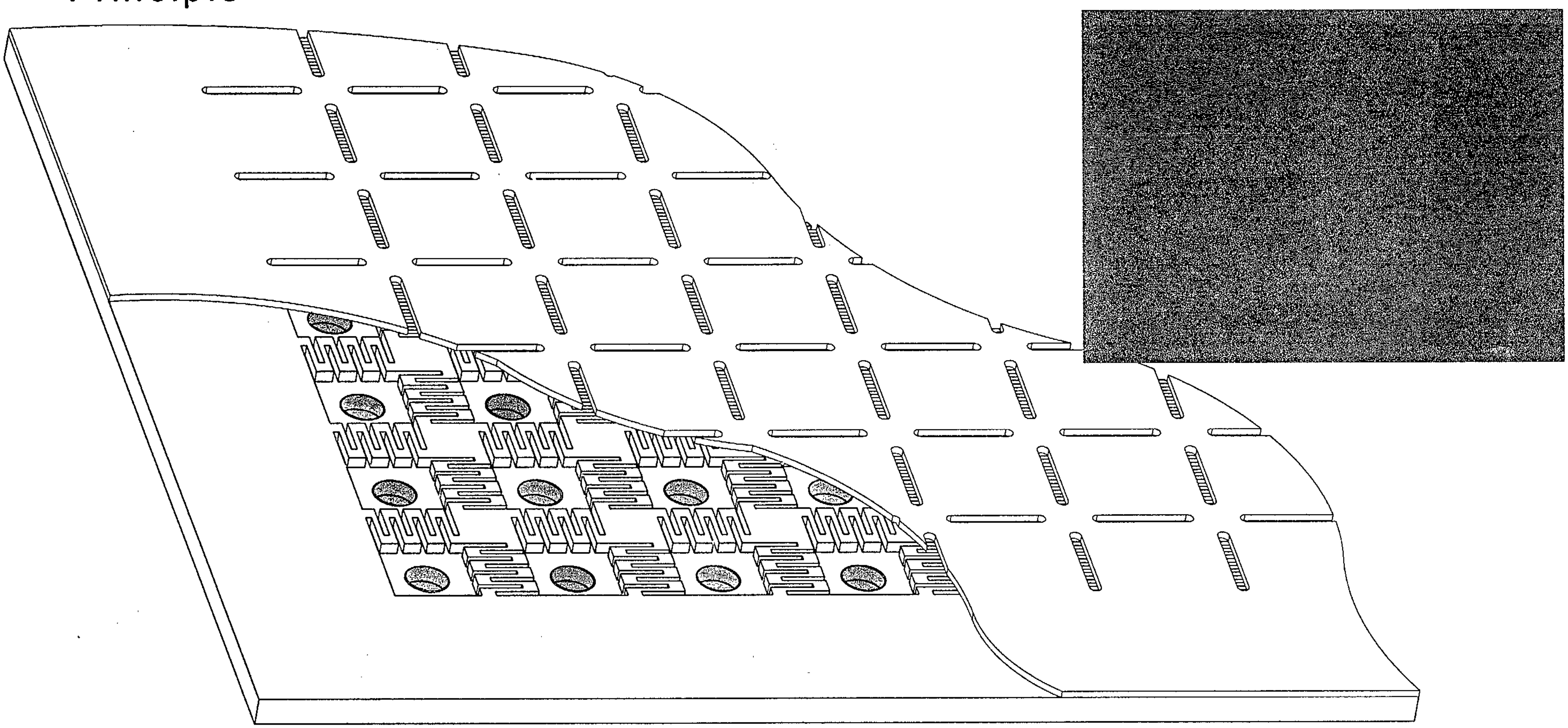
HIGH THROUGHPUT MICRO MIXER

Principle



Mask pattern

1560 mixing cells per micro mixer

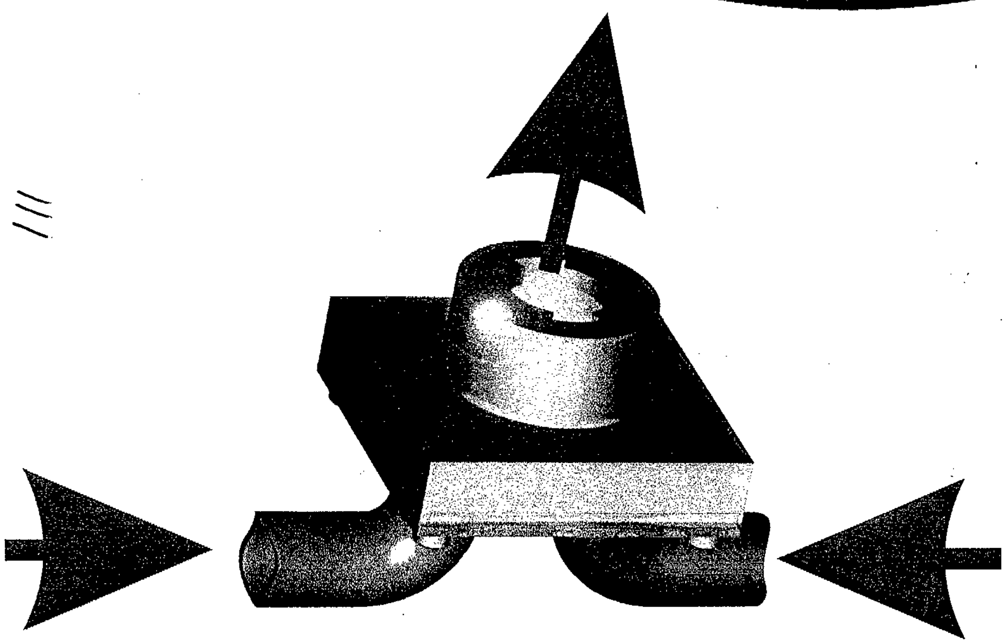
E 90342

110

HIGH THROUGHPUT MICRO MIXER

700 l/h

185 gallons/h



Size: 50 mm x 50 mm x 12.5 mm

E 90341

Integrated Reaction, Separation, and Detection Systems for Biochemical Analysis

Students: Sundaresh N. Brahmasandra,* Kalyan Handique,* Madhavi Krishnan,* Piu F. Man,** Vijay Namasivayam,* Sethu Palaniappan,** Timothy S. Sammarco,* James R. Webster,**

Staff: Dylan Heldsinger,* Brian N. Johnson,* Darren Jones,***

Faculty: Mark A. Burns,* David T. Burke,*** and Carlos H. Mastrangelo**

*Department of Chemical Engineering

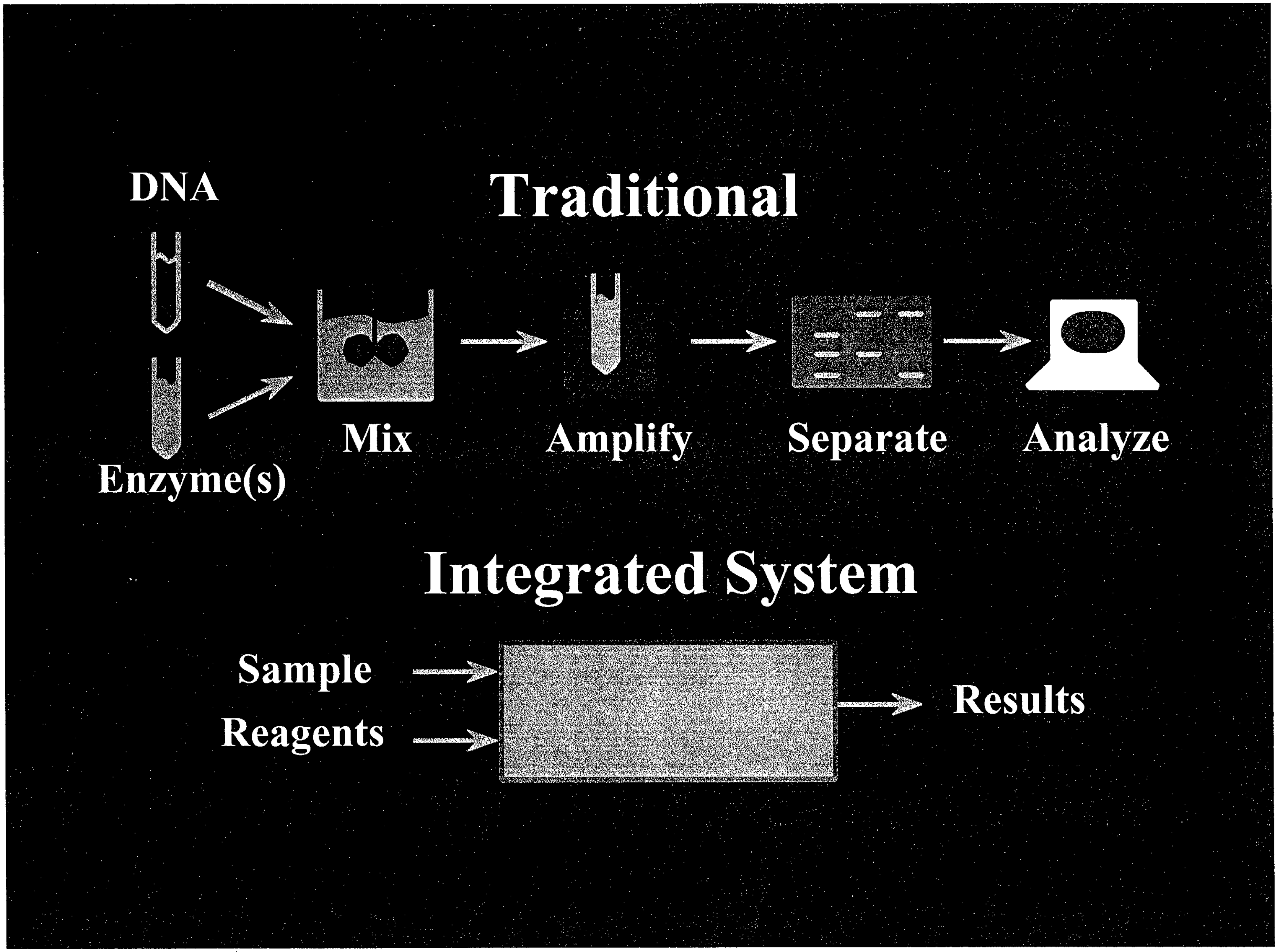
**Department of Electrical Engineering

***Department of Human Genetics

Support:

NIH, DARPA, Becton Dickinson,

University of Michigan


Traditional
DNA
Enzyme(s)
Mix
Amplify
Separate
Analyze
Integrated System
Sample
Reagents
Results

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Motivation

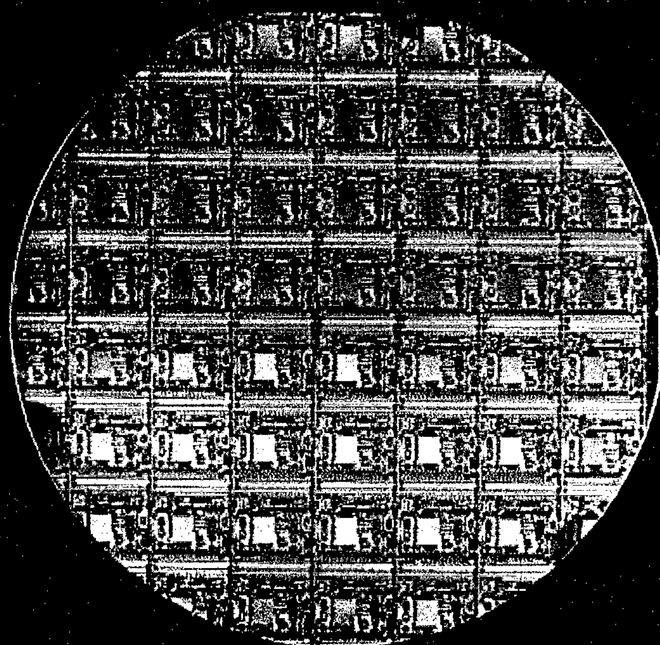
Human Genome Project

- Sequence the entire human genome
- Technology developments needed
- Increase demand for genetic information

DNA genotyping/sequencing applications

- Medical Diagnosis
- Forensic Analysis
- Agricultural Industry
- Many others

Miniaturization and Integration



- Low reagent costs
- Batch production techniques
- Low cost devices disposable: no contamination
- Self-contained: minimal external equipment

Integrated Devices

- All components must be compatible
- Simple designs necessary
- Best component not always used
- Changes affect all components
- Standard chemistries used

Microfluidics

Solute motion:

- Electroosmotic
- Individual Drops
- Continuous/ batch

Channel material:

- Glass
- Silicon
- Polymer
- Hybrid/Monolithic construction

Reaction Systems

Physical:

- Metal/Si heater
- Continuous/batch
- Isothermal/cycle
- Immobilize/solution

Chemical:

- Restriction digestion
- Amplification
- Sanger reaction
- Other enzymatic reaction
- Other reaction

Separation Systems

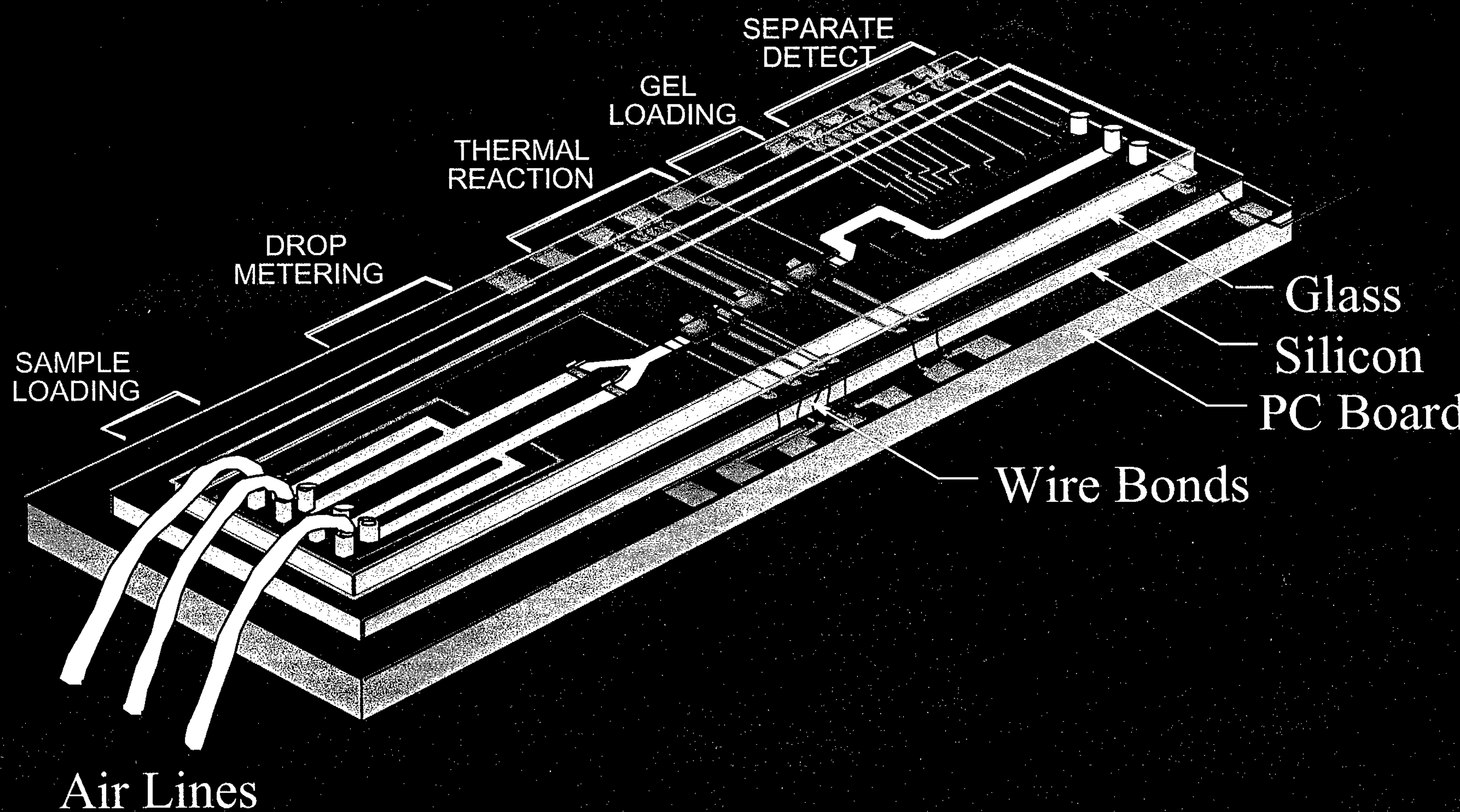
Separation:

- Capillary
- Etched channel
- Molded substrate
- Crosslinked gel
- Solution

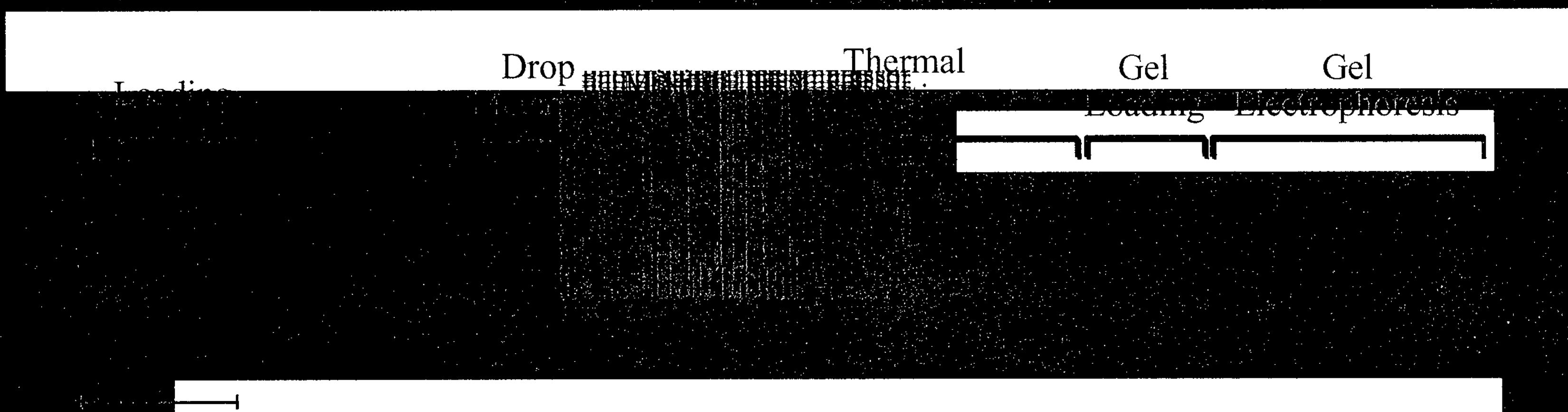
Detection:

- Fluorescence
- Radiation
- Electrochemical
- Electrochemi-
  luminescence

Integrated DNA Analysis

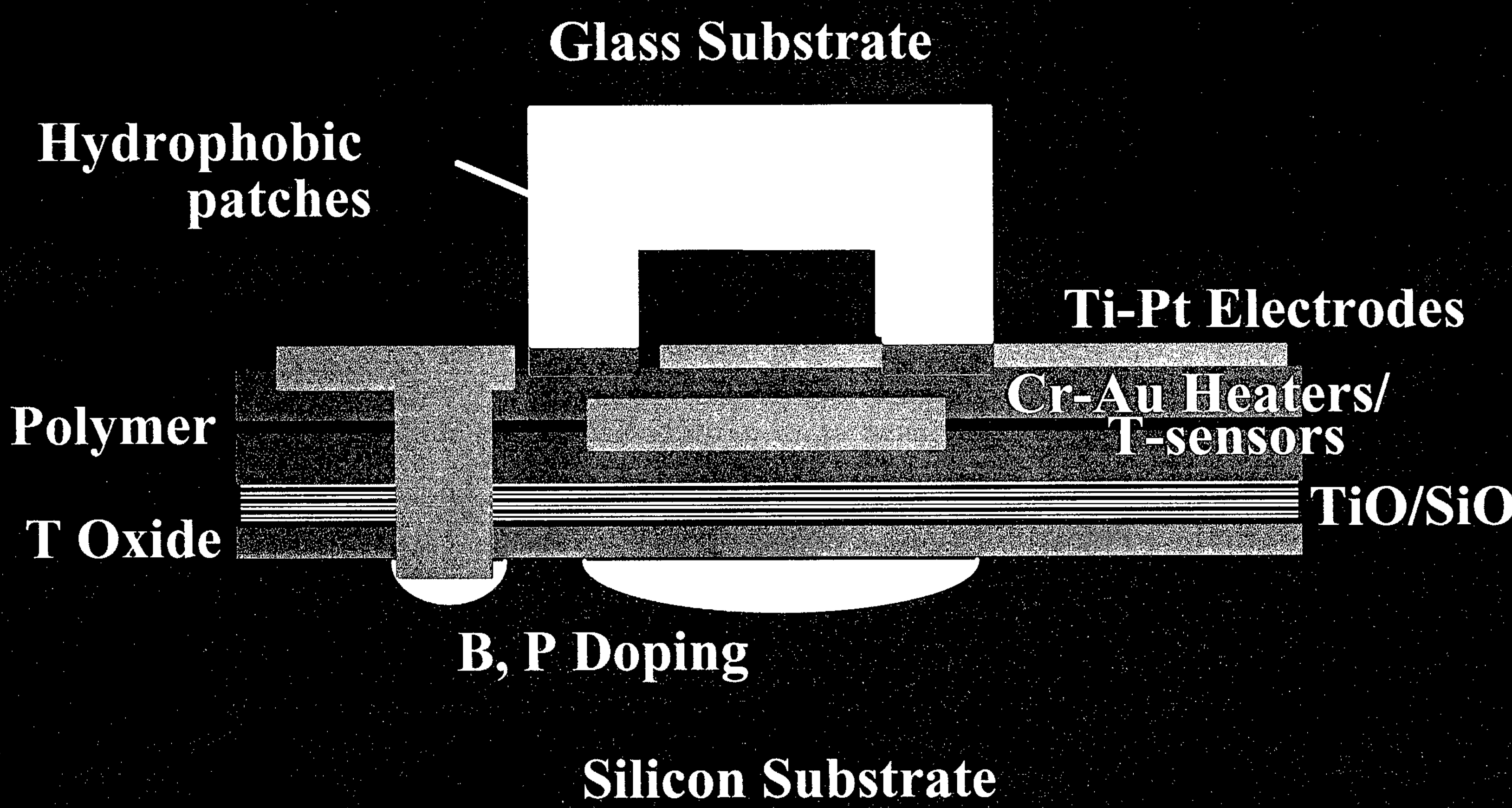


Si/Glass Device

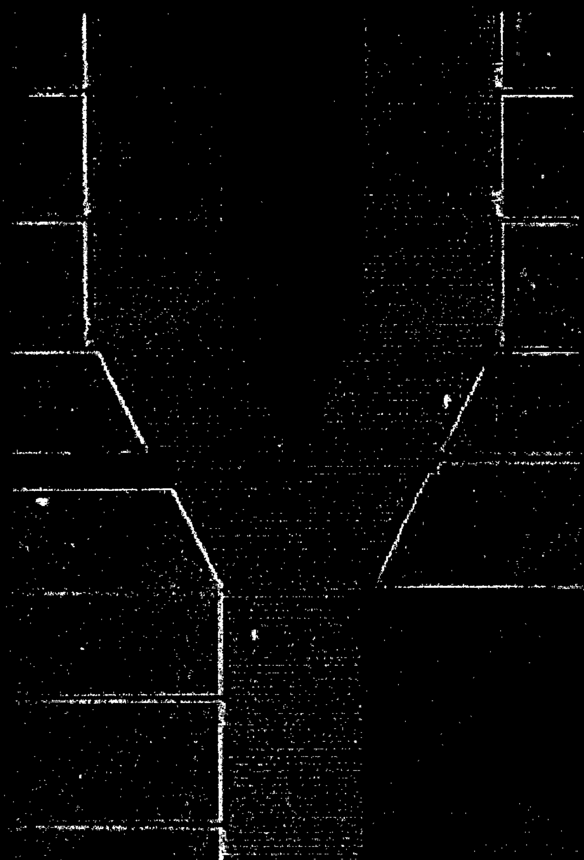


- Individual Drops (~100 nl)
- Integrated Heating (± 0.1 C)
- Integrated Detection (10 ng/μl)

Device Construction

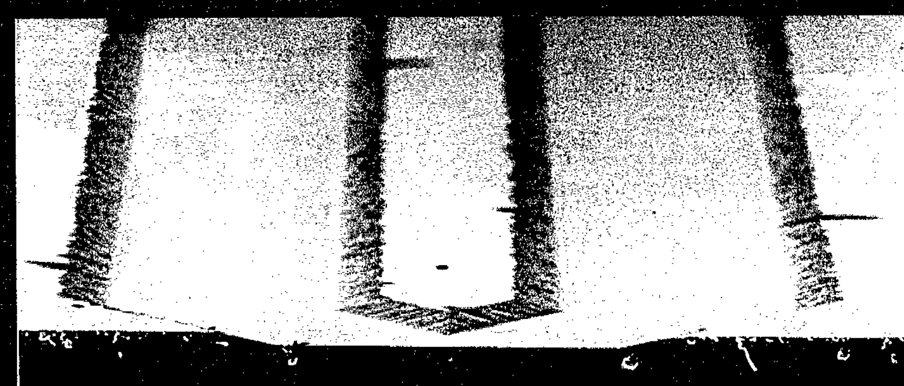


Device Construction



Fabricated
Heater

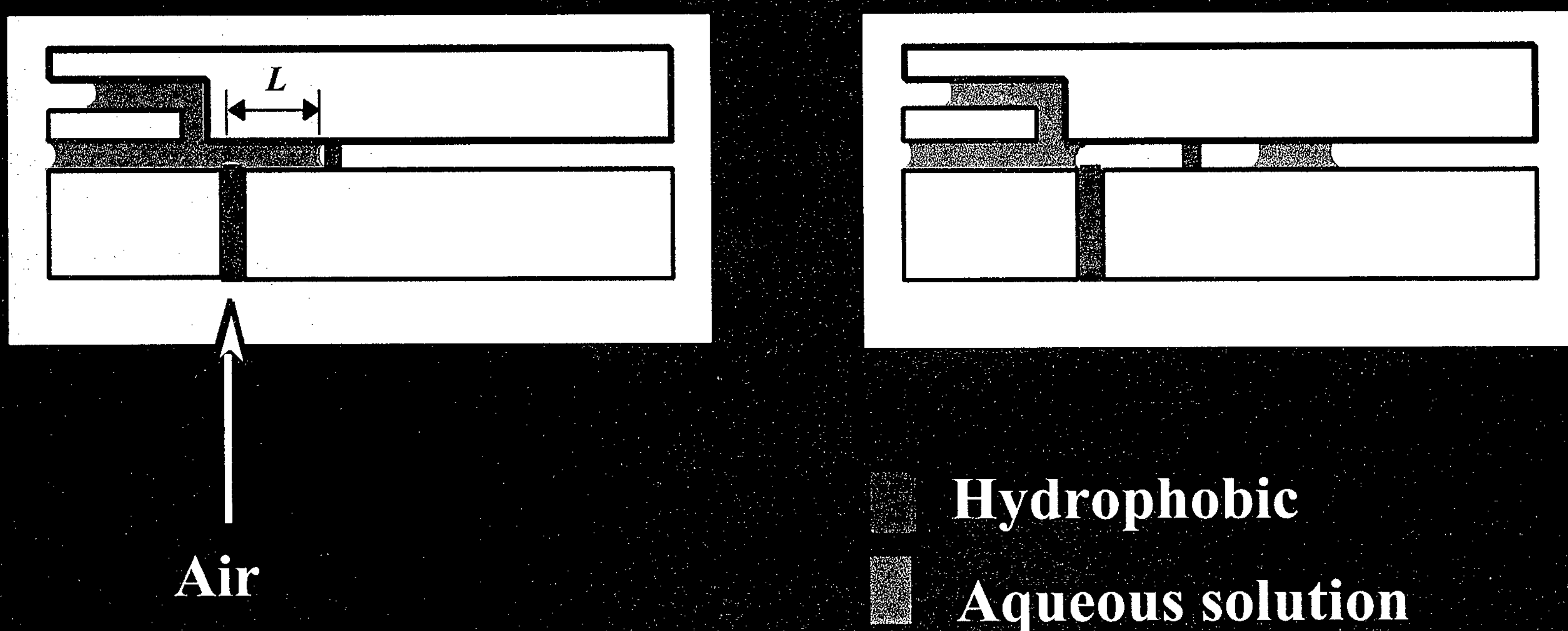
Etched
Glass



Integrated Device

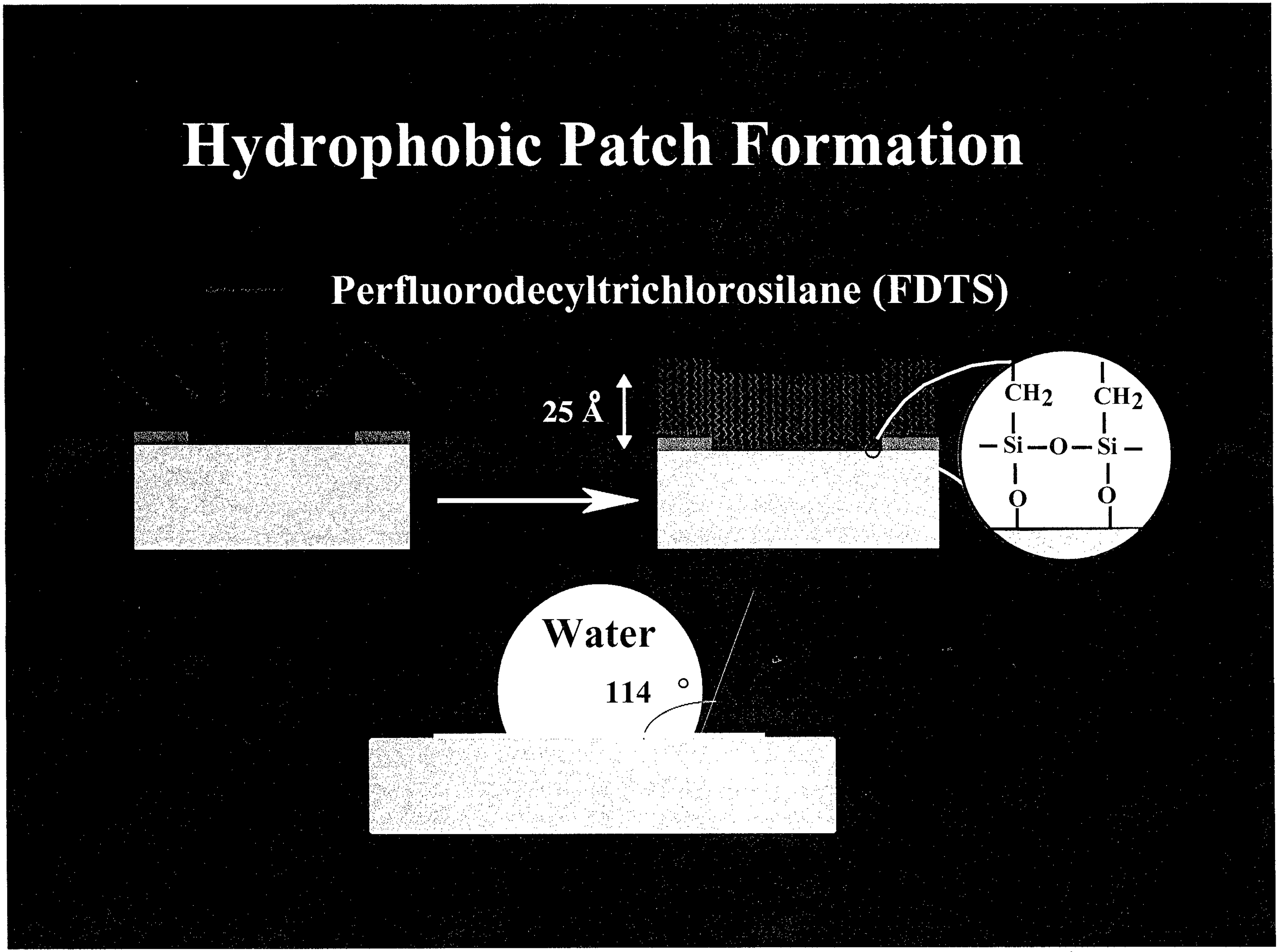
- Reaction
- Separation/detection
- Integration

Reagent Metering

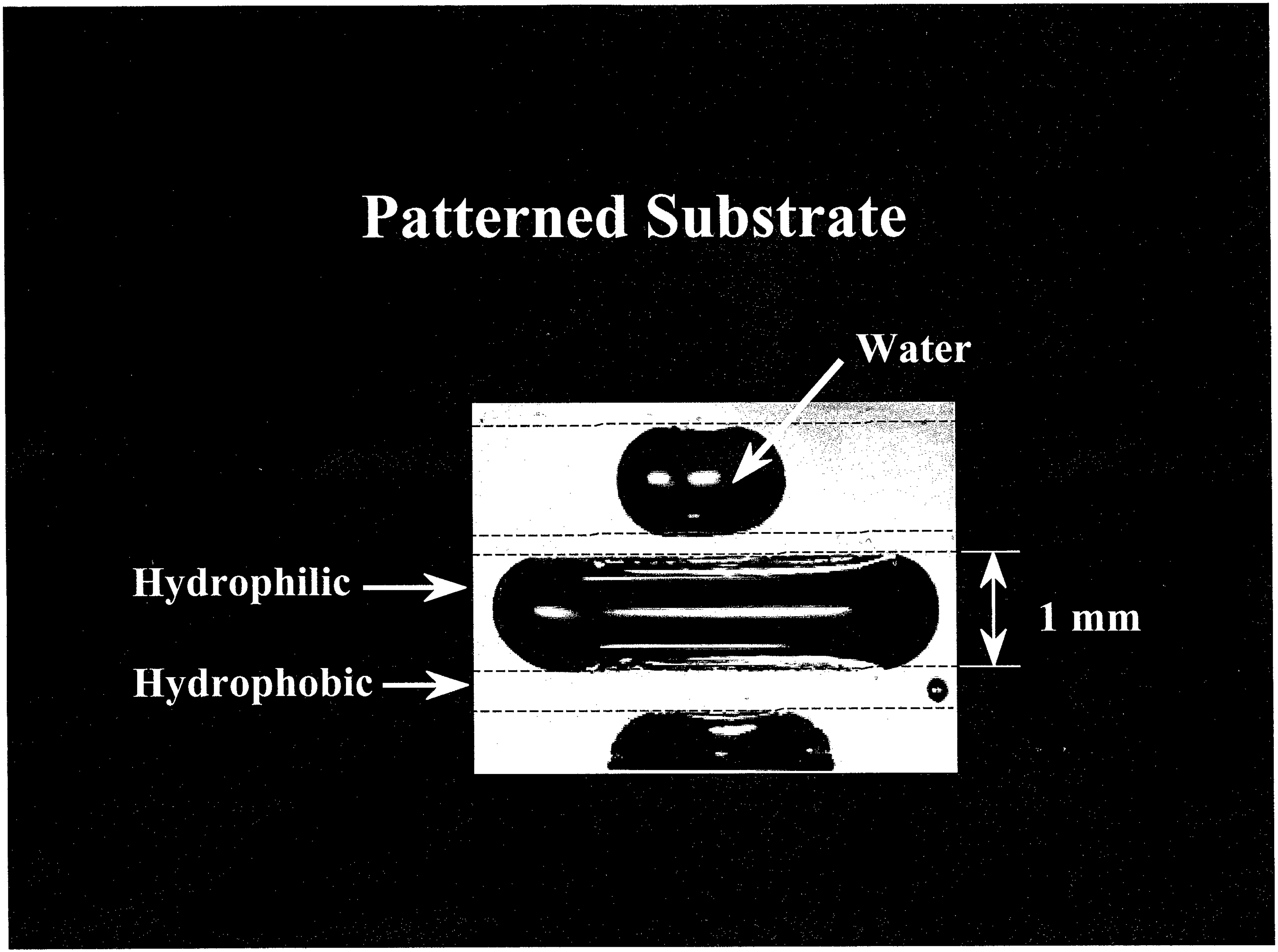


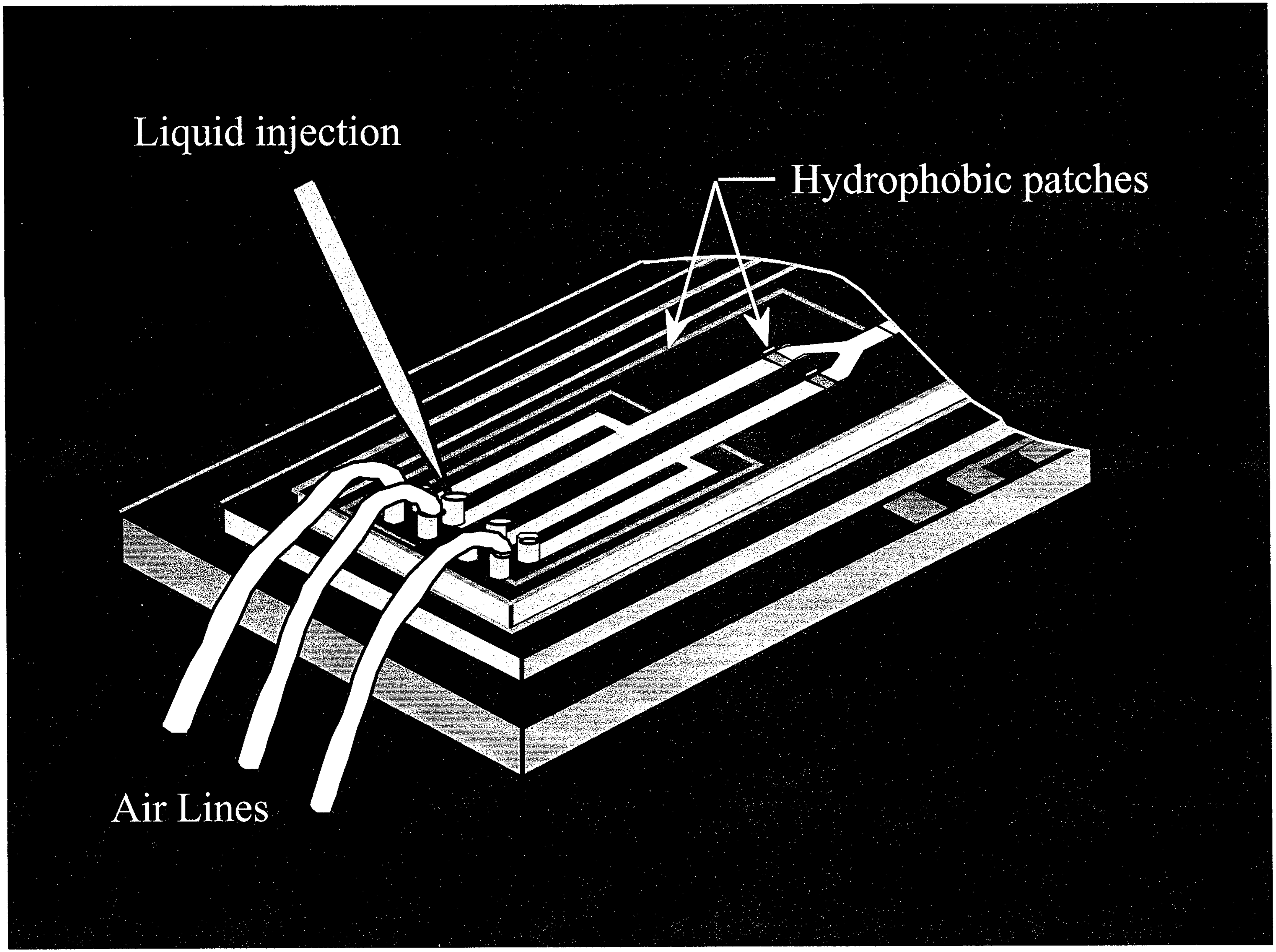
Volume range: 1 - 100 nl

(*Based on channel cross-section and L*)

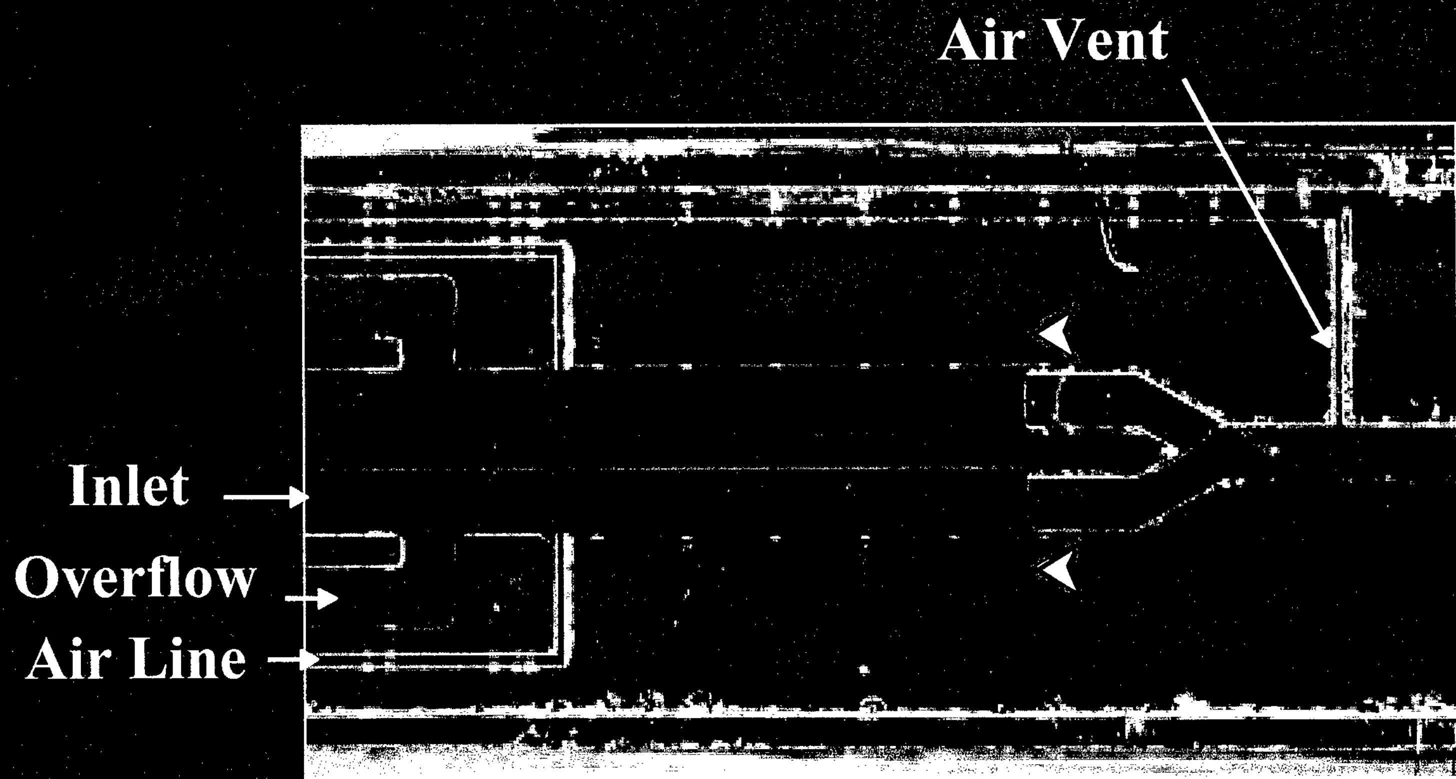

Hydrophobic Patch Formation
Perfluorodecyltrichlorosilane (FDTS)
25 Å
CH2
CH2
Si
O
Si
O
O
Water
114 °

126

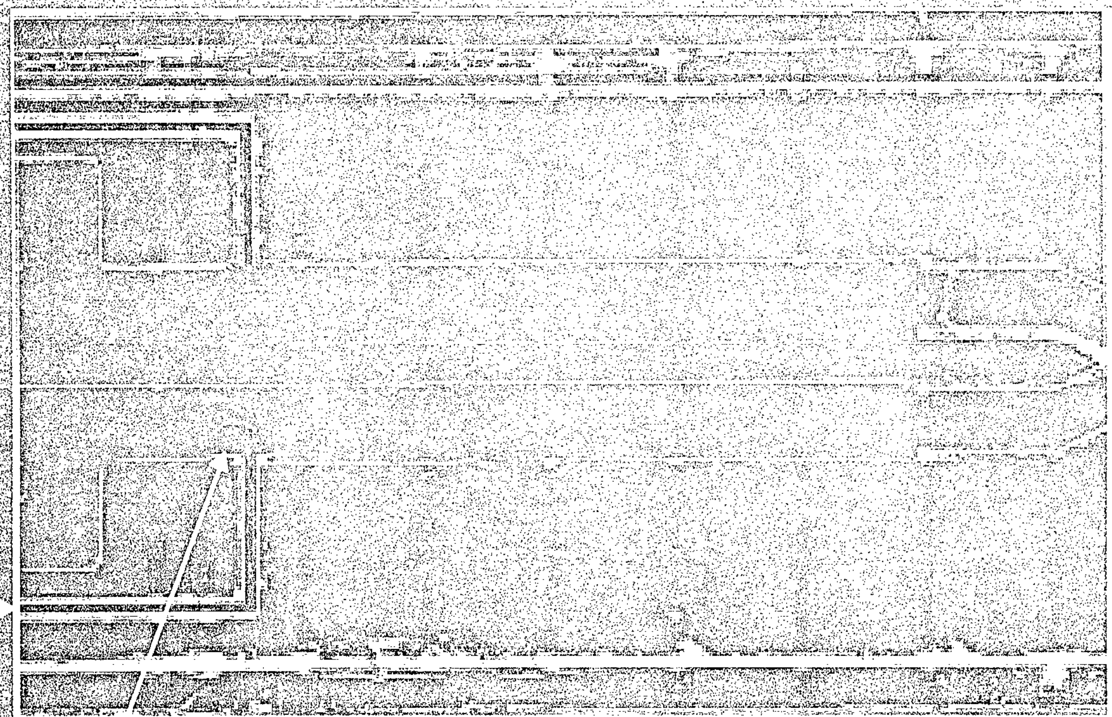

Patterned Substrate
Water
Hydrophilic
Hydrophobic
1 mm


Liquid injection
Hydrophobic patches
Air Lines

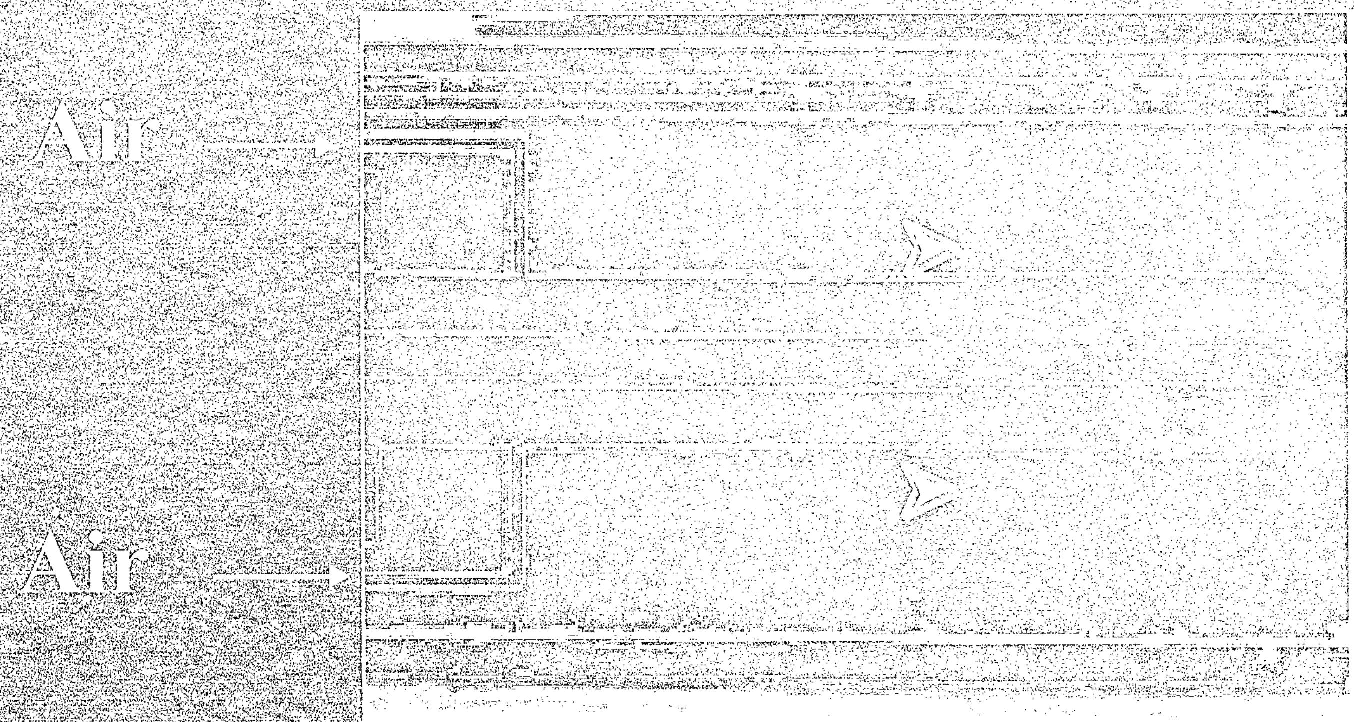
Meter 120 nl reagents



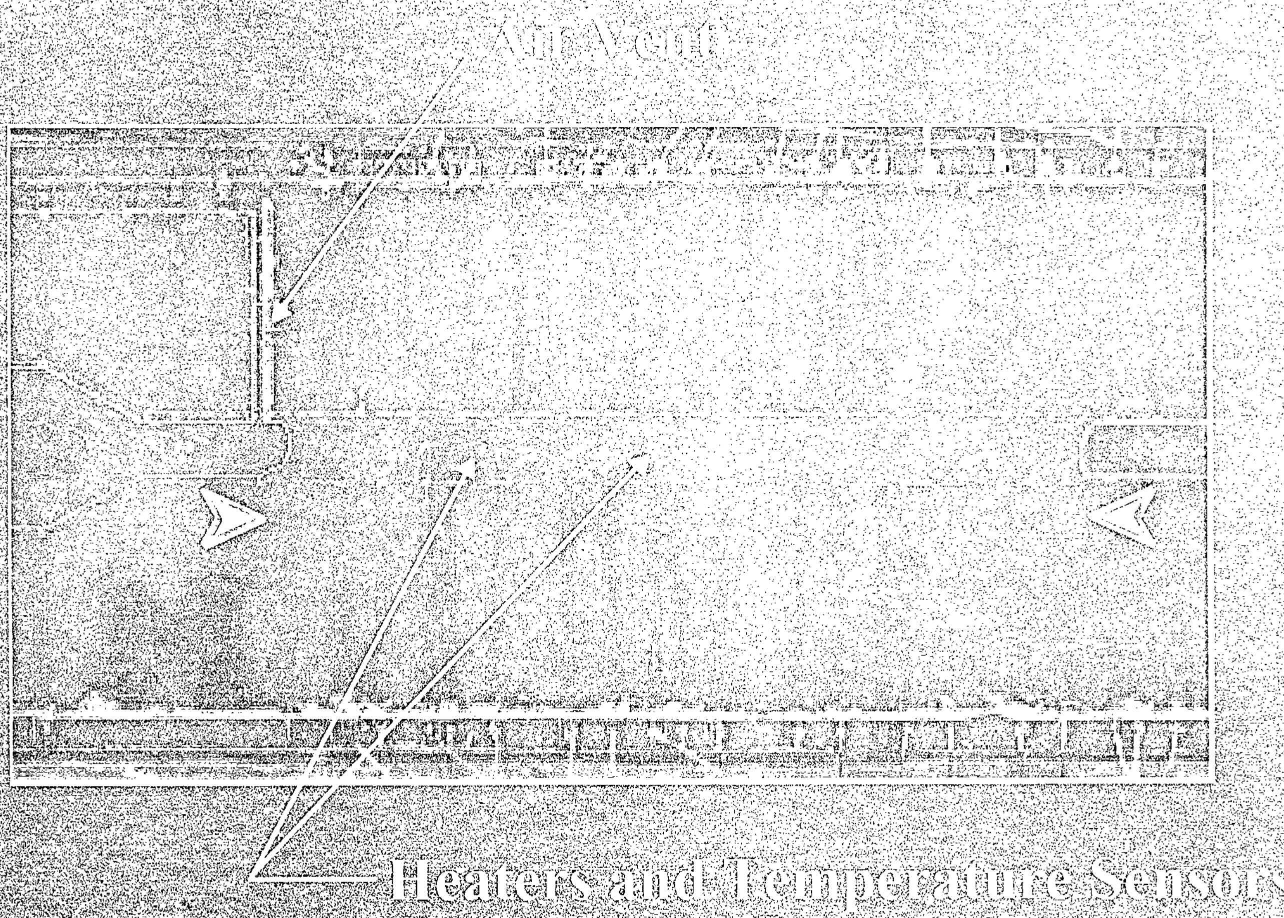
Meter 120 nl reagents



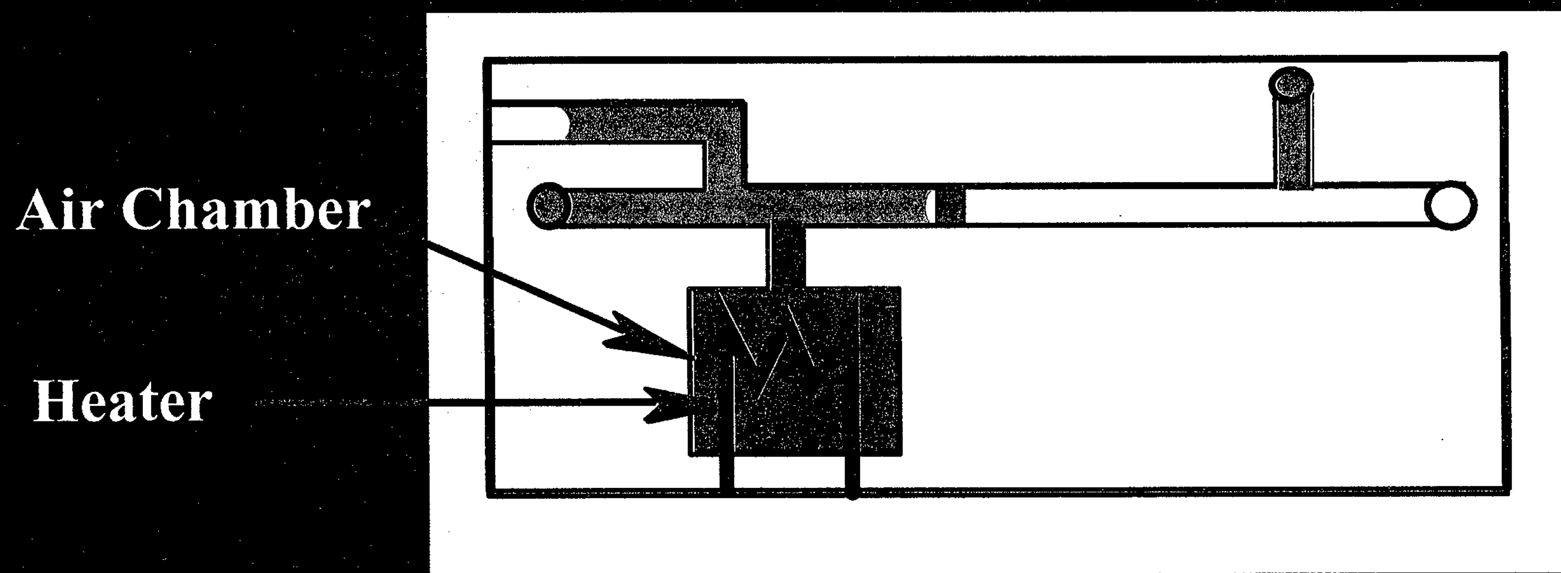
Meter 120 nl reagents



240 nl Reaction Volume

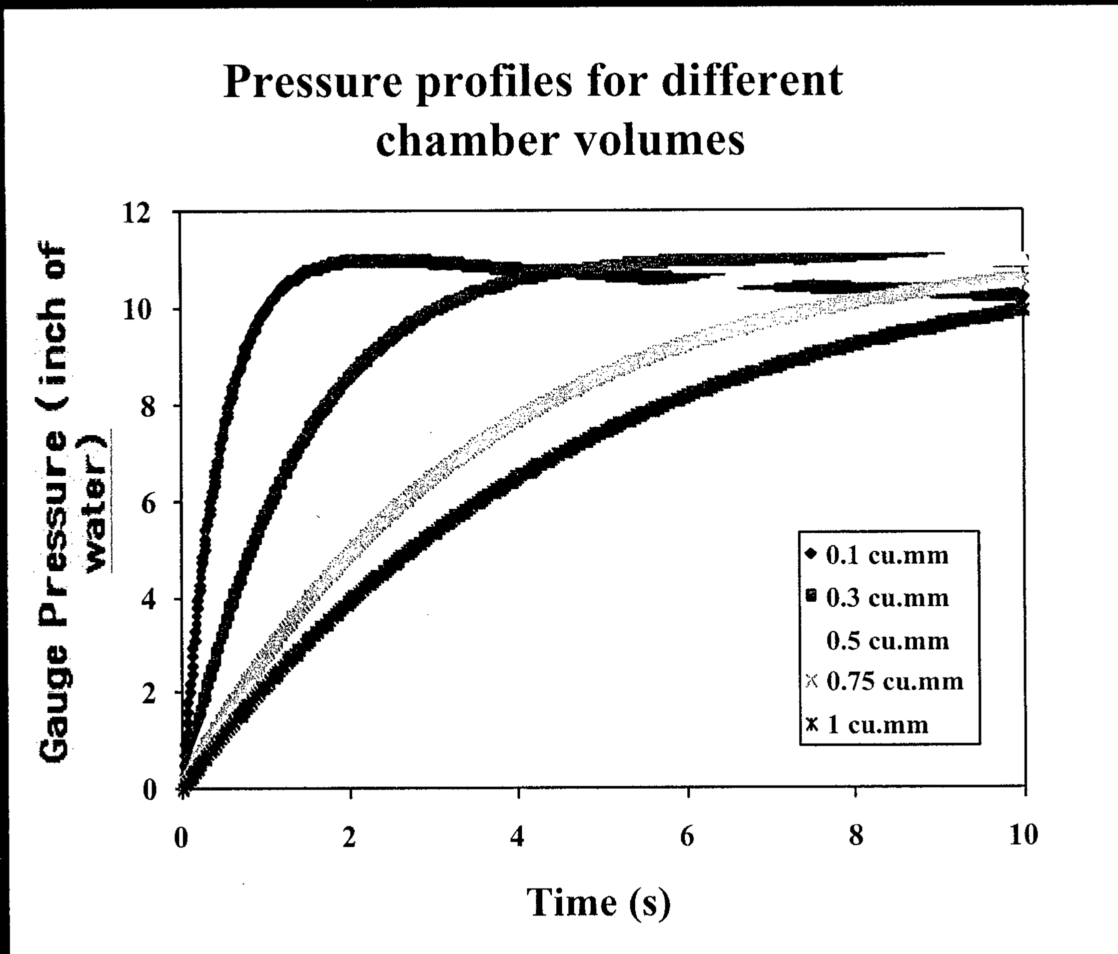


On-Chip Pressure generation

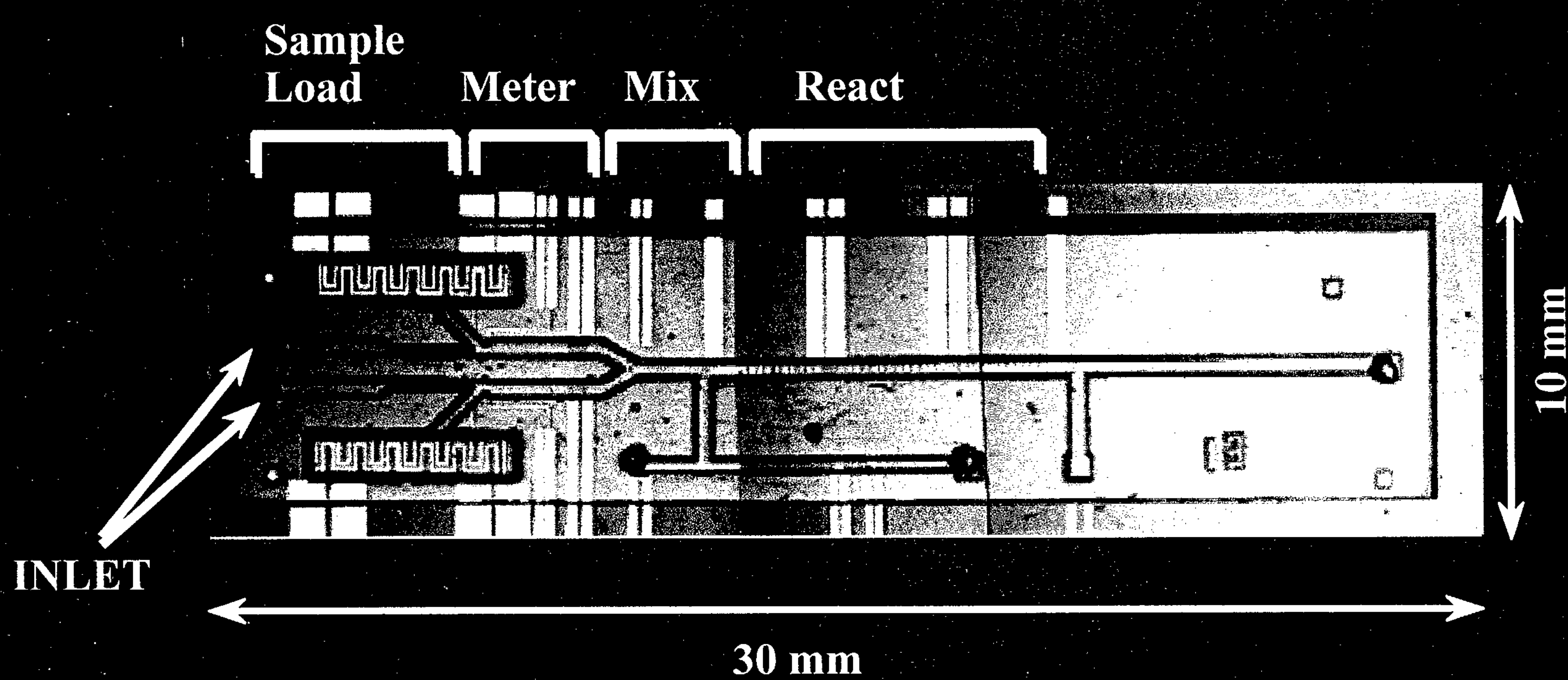


$T \uparrow \Rightarrow P \uparrow$

On-Chip Pressure generation



Internal Pressure Increase



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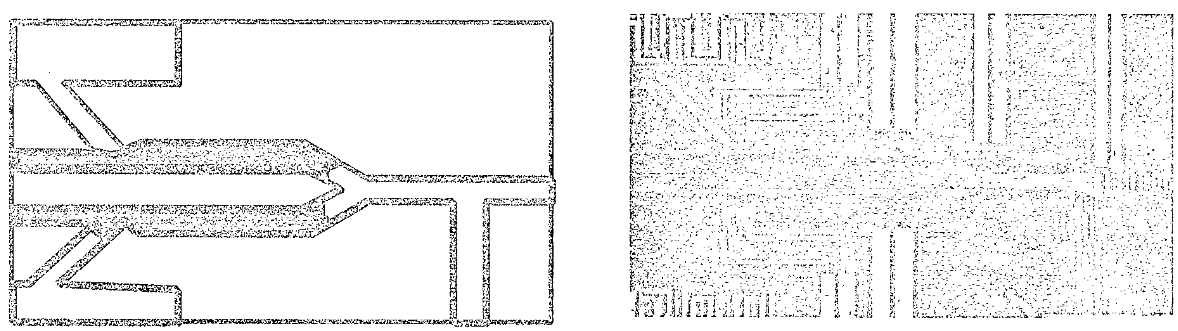
Meter and Position

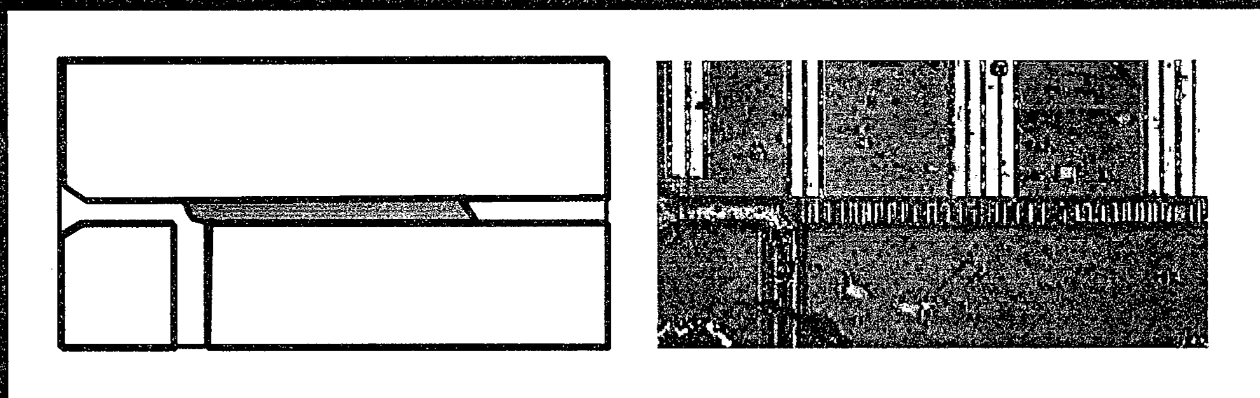


- ~1 µl DNA Sample
- ~1 µl Enzyme Sample

$$\Delta P = \gamma_{LV}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

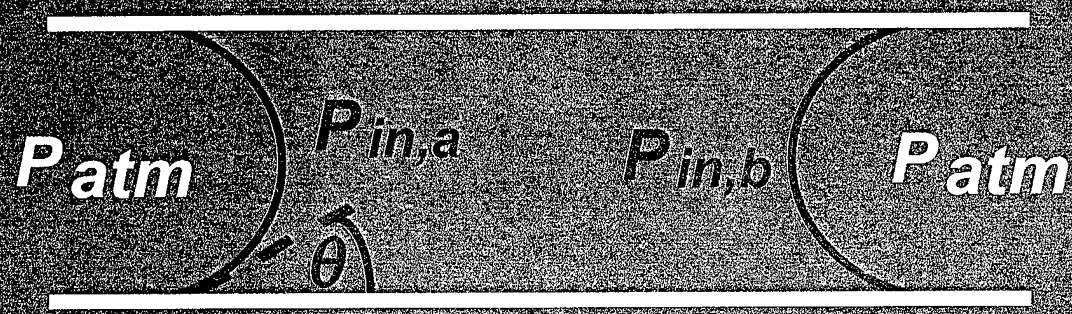
- γ affected by T

$$\gamma_{LV} = a - bT$$



Drop positioned in reaction section

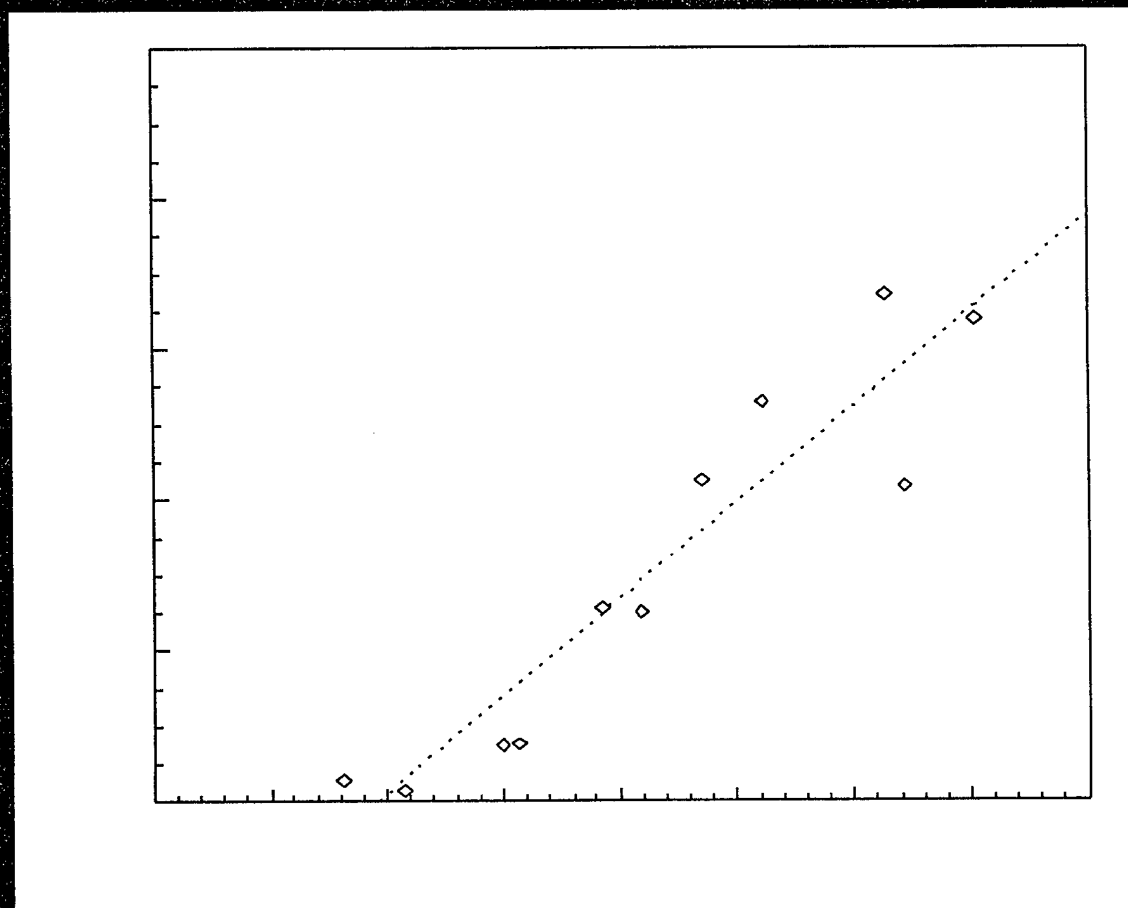
Surface Forces



- $P_{in} < P_{atm}$
- If $P_{in,a} > P_{in,b}$, motion to right
- Change ²P across interface

Drop Motion by Resistive Heating

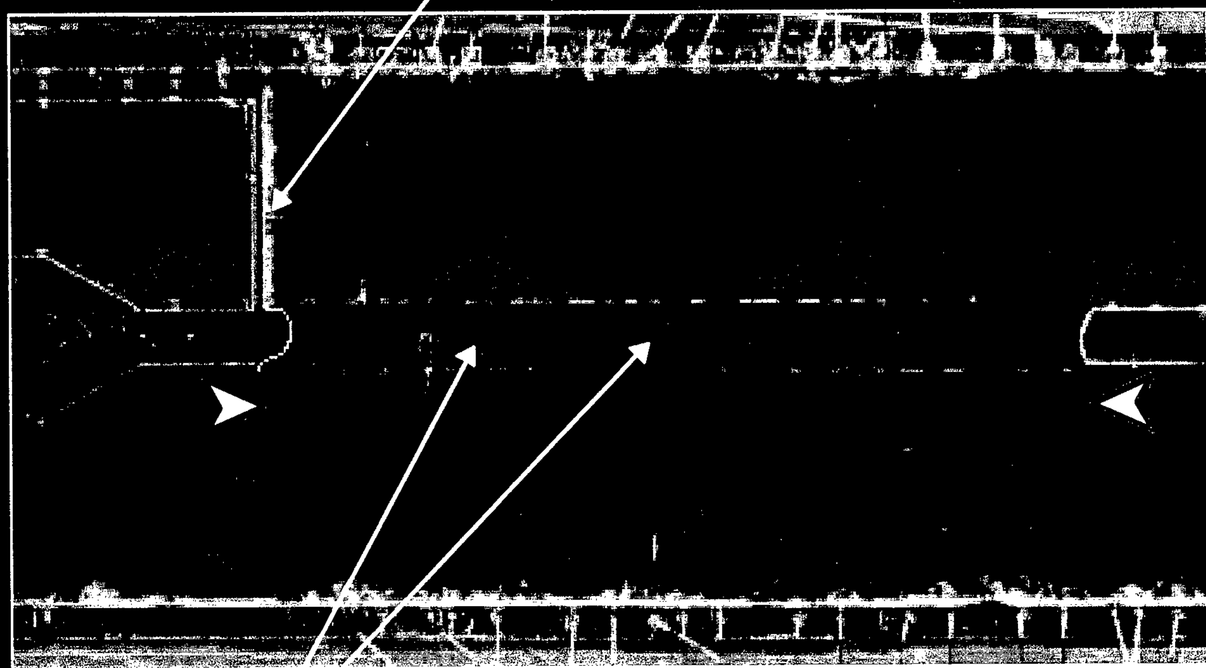
Drop velocity vs. temperature



Integrated Device

- Microfluidics
- Reaction
- Separation/detection
- Integration

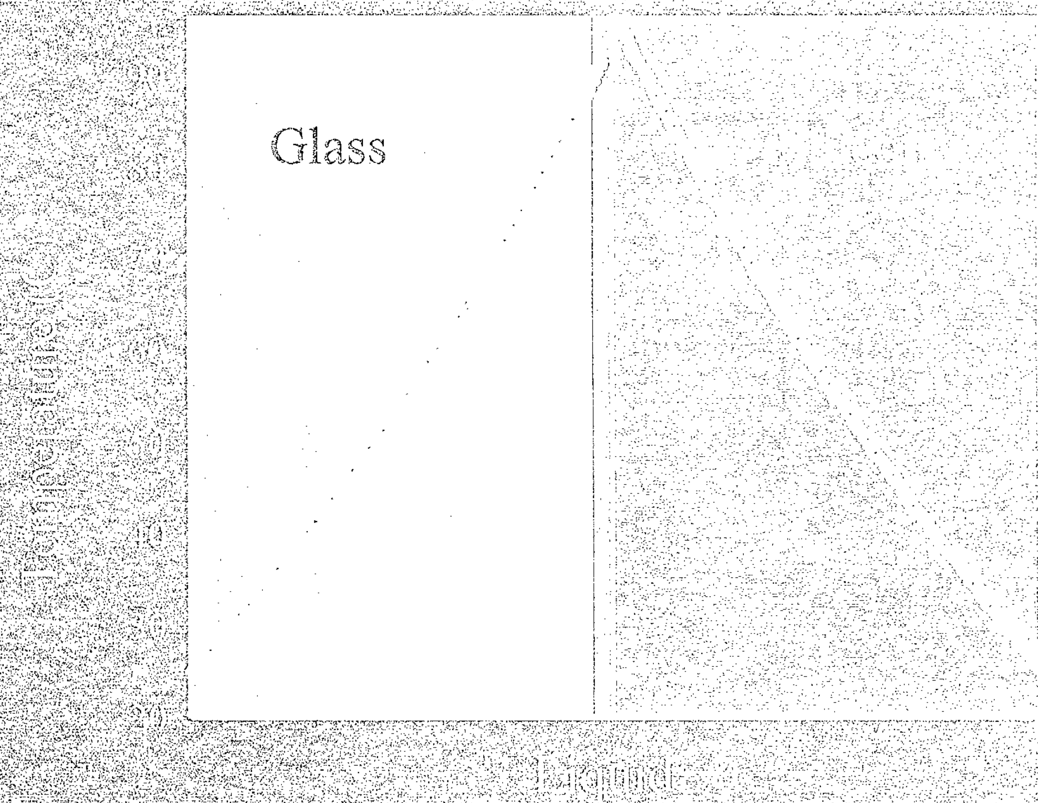
240 nl Reaction Volume



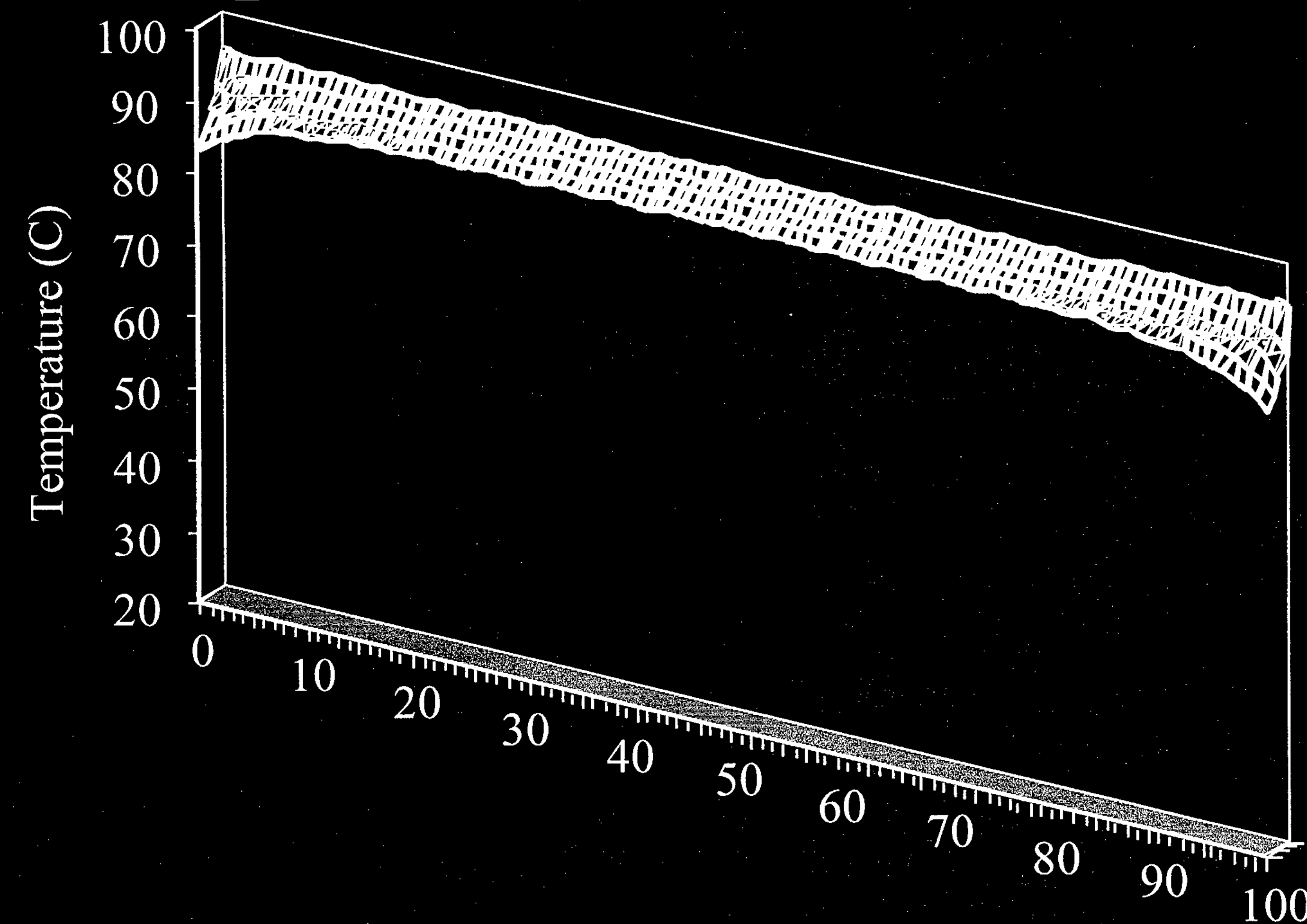
Physical: Temperature

- Rapid temperature cycling
- Precise/accurate temperature control
- Uniform temperature profile

Device temperature profile



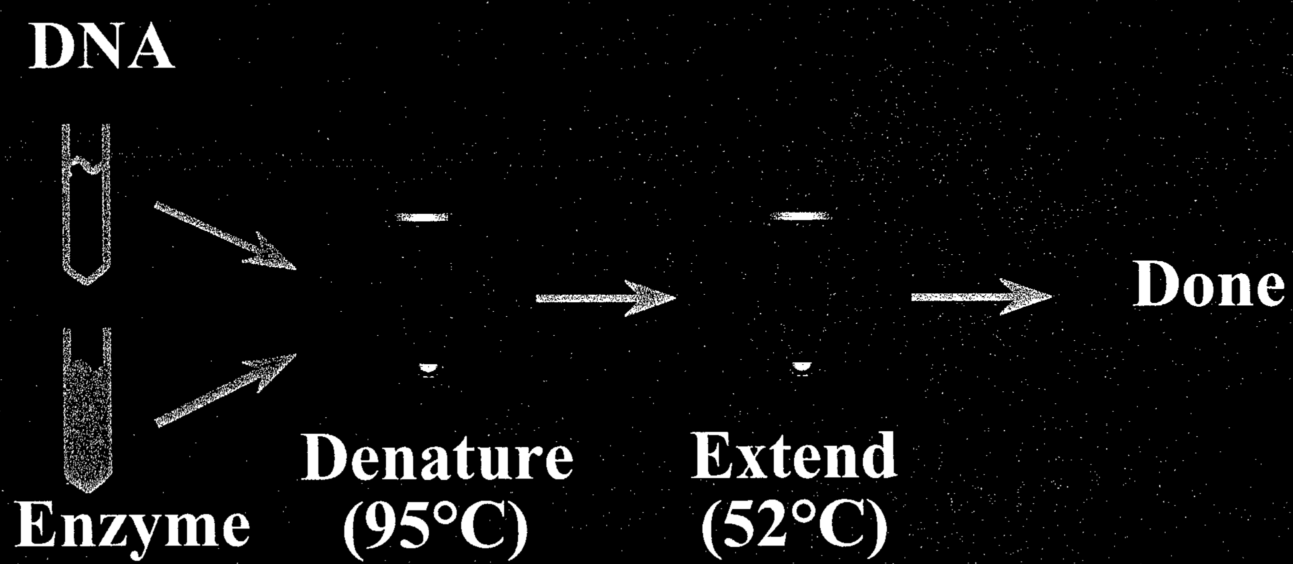
Liquid temperature profile

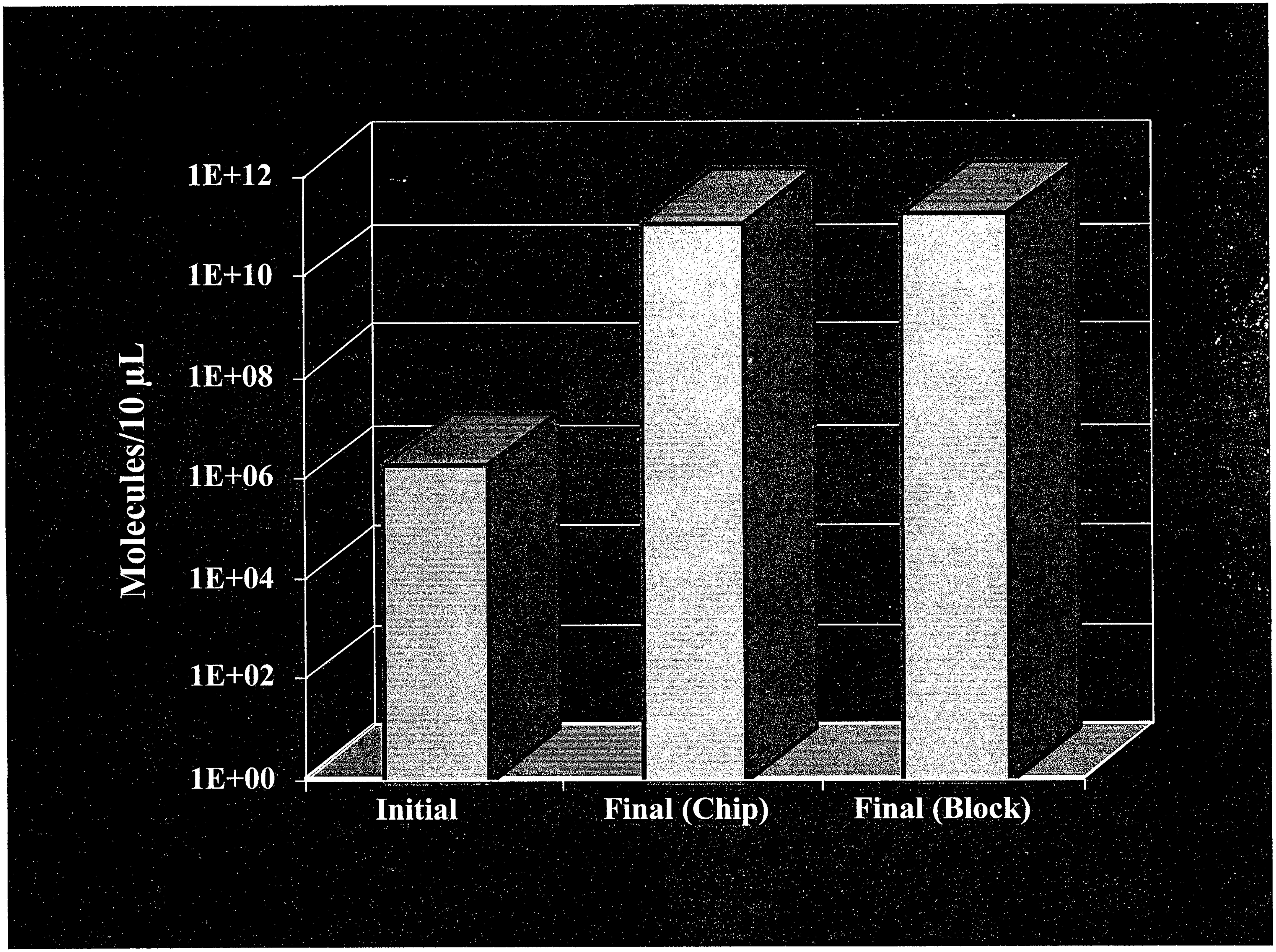


Chemical: Surfaces

- Many surface/materials exposed
- High surface-to-volume ratio
- Leaching of chemicals into solution
- Adsorption of enzymes/DNA onto surface
- BSA coating effective

Strand Displacement Amplification (SDA)

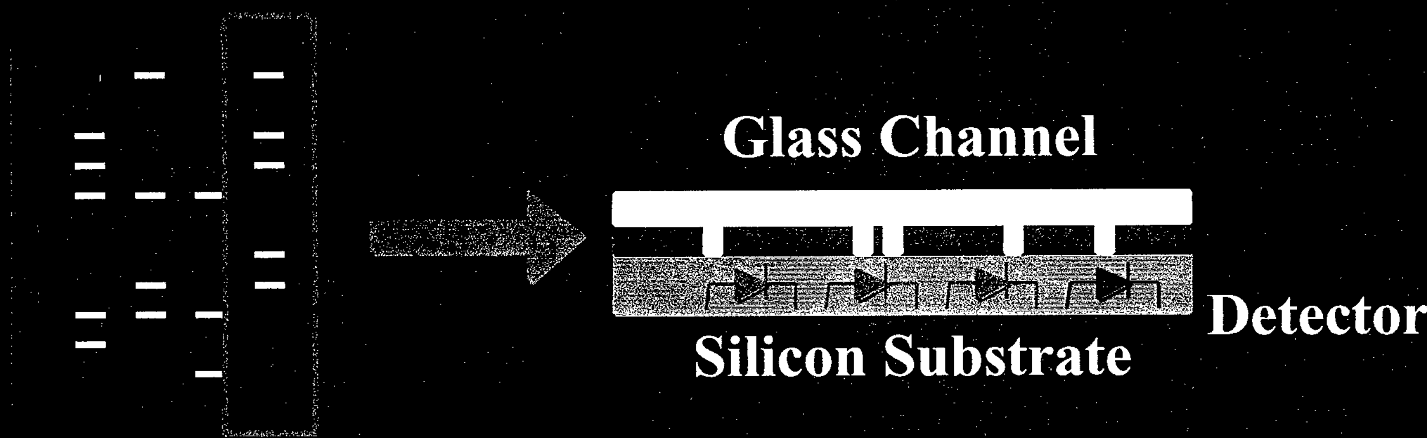



Molecules/10 µL
1E+12
1E+10
1E+08
1E+06
1E+04
1E+02
1E+00
Initial
Final (Chip)
Final (Block)

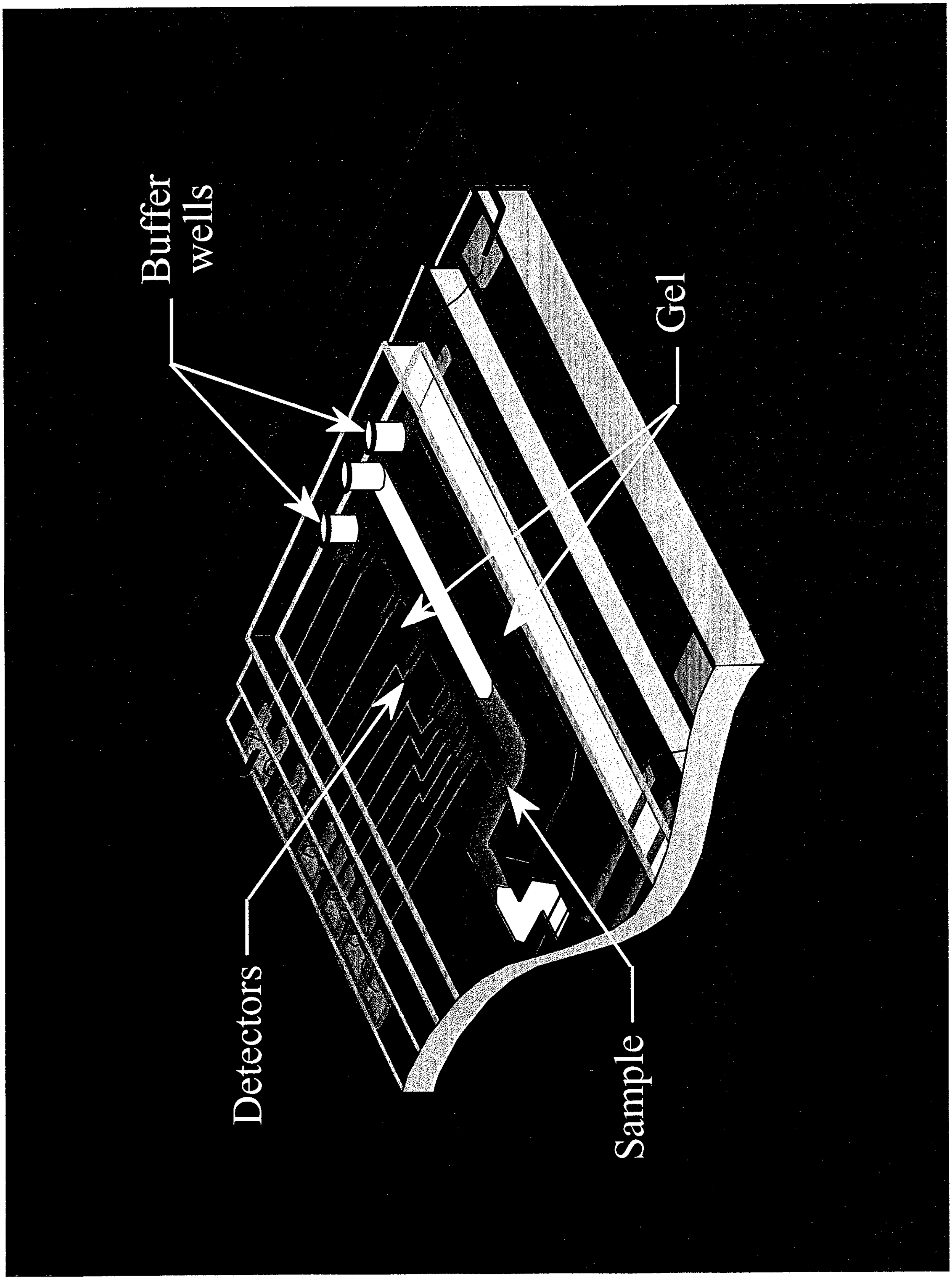
Integrated Device

- Microfluidics
- Reaction
- Separation/detection
- Integration

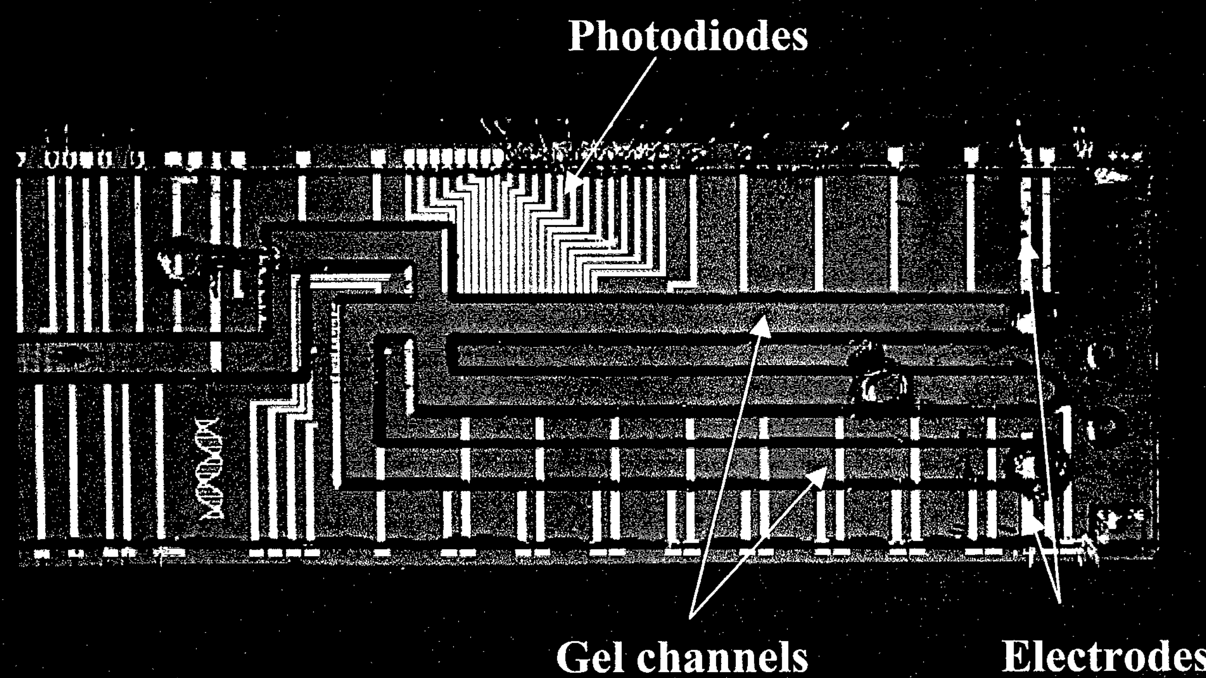
Microfabricated Separation and Detection



- Similar thickness as current gels
- Detectors "touching" bands
- Multiple detectors possible


Buffer
wells
Gel
Detectors
Sample

Microfabricated Device: Photo

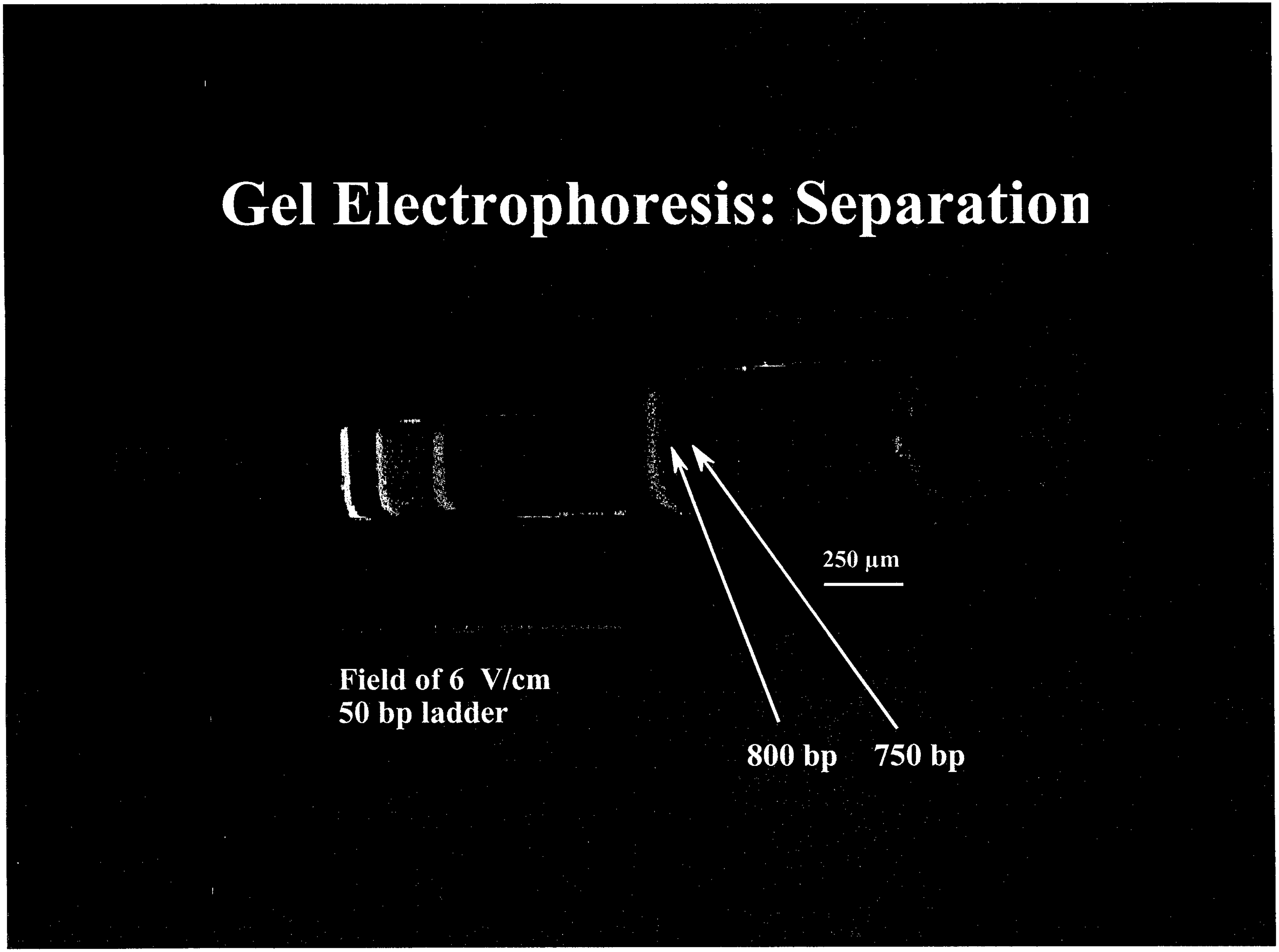


Gel Electrophoresis: Loading

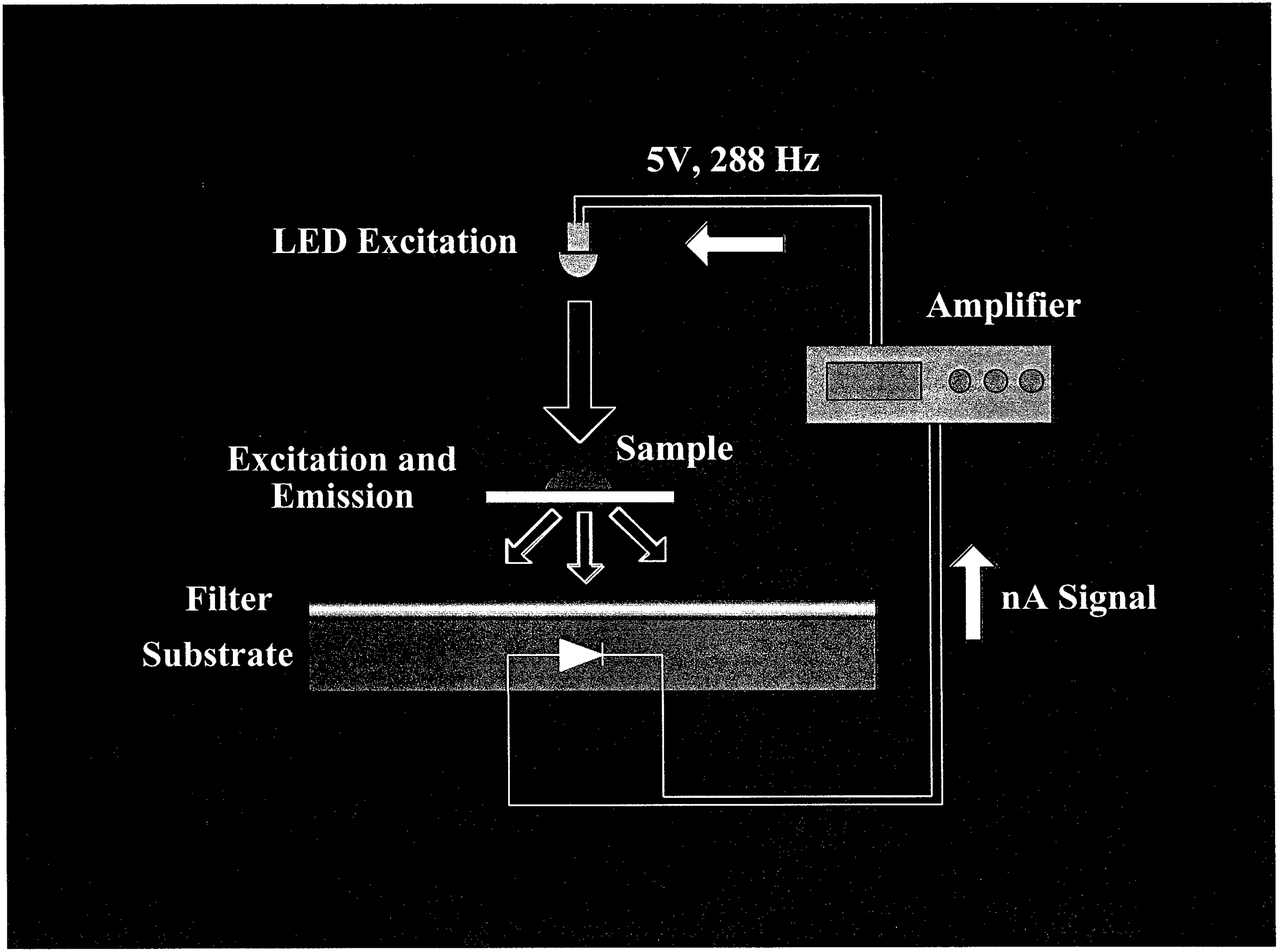
Sample in intersection

10 s compaction

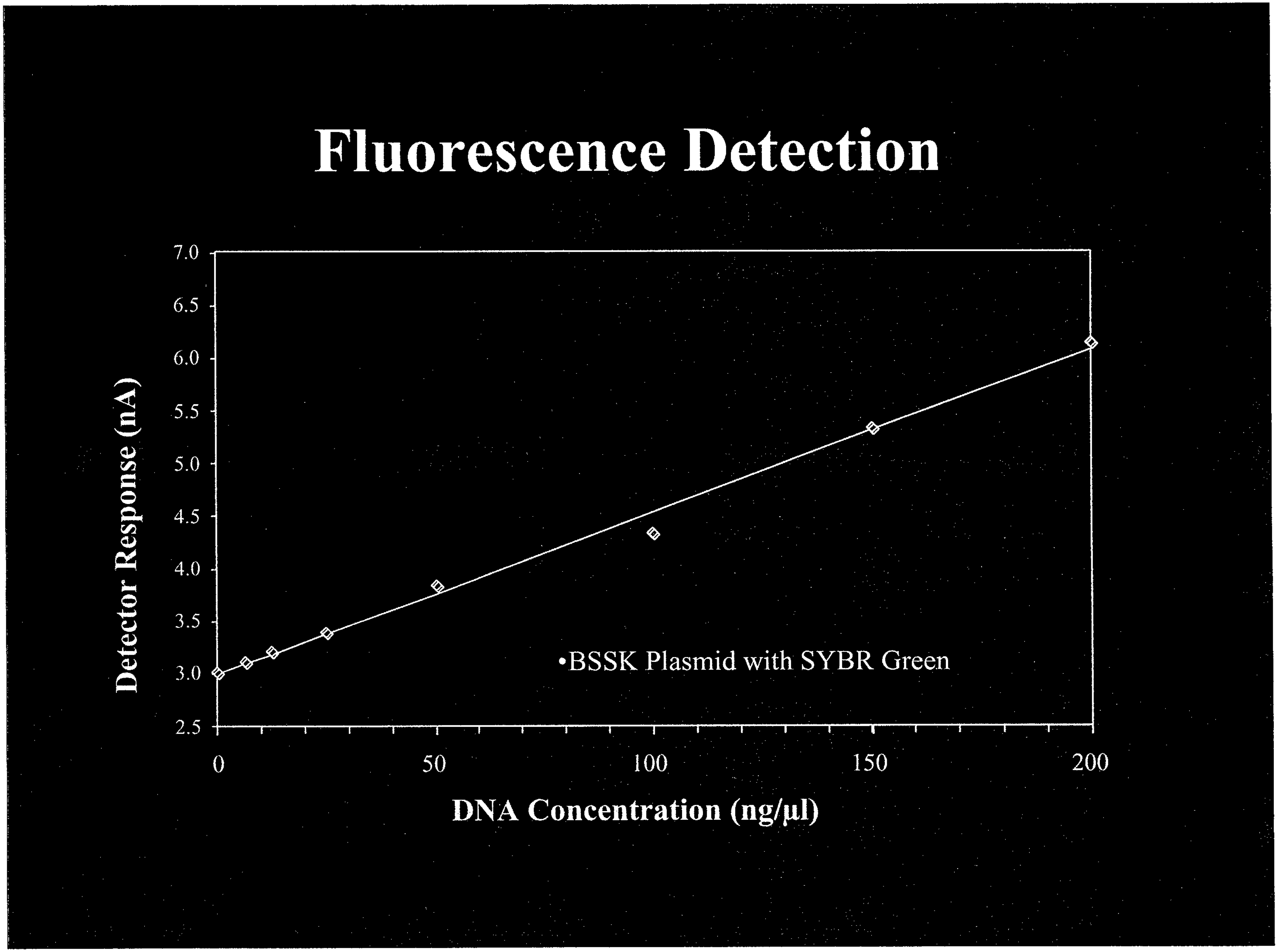
Remove excess



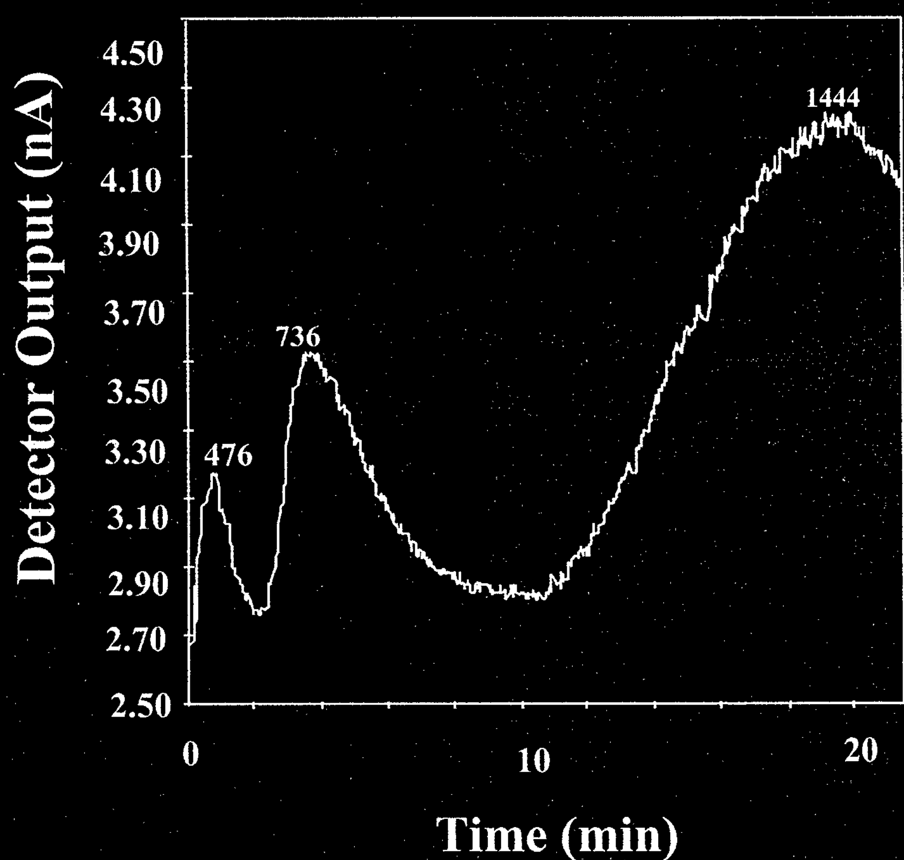
Gel Electrophoresis: Separation
250 μm
Field of 6 V/cm
50 bp ladder
800 bp
750 bp



5V, 288 Hz
LED Excitation
Amplifier
Excitation and
Emission
Sample
Filter
Substrate
nA Signal


Fluorescence Detection
Detector Response (nA)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
0
50
100
150
200
DNA Concentration (ng/µl)
•BSSK Plasmid with SYBR Green

On-Chip Detection



- pUC19 + Taq 1 Digest
- SYBR Green labeled

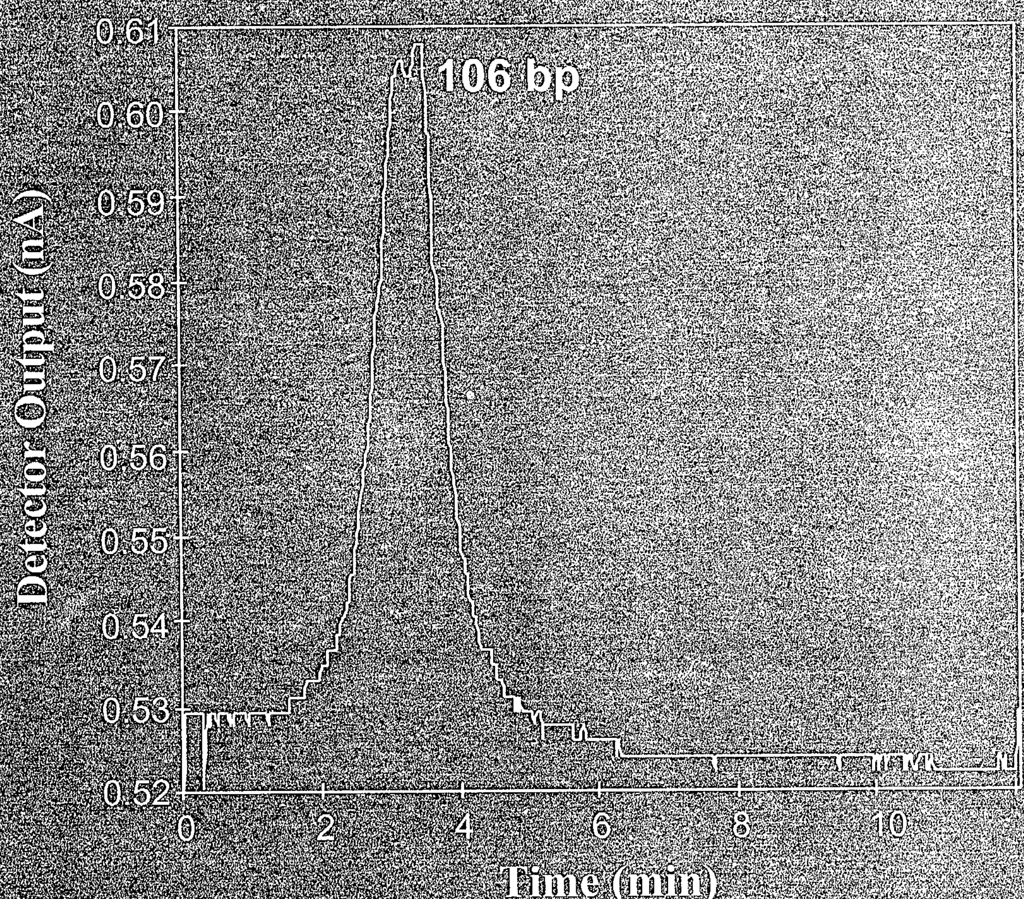
Integrated Device

- Microfluidics
- Reaction
- Separation/detection

Integration

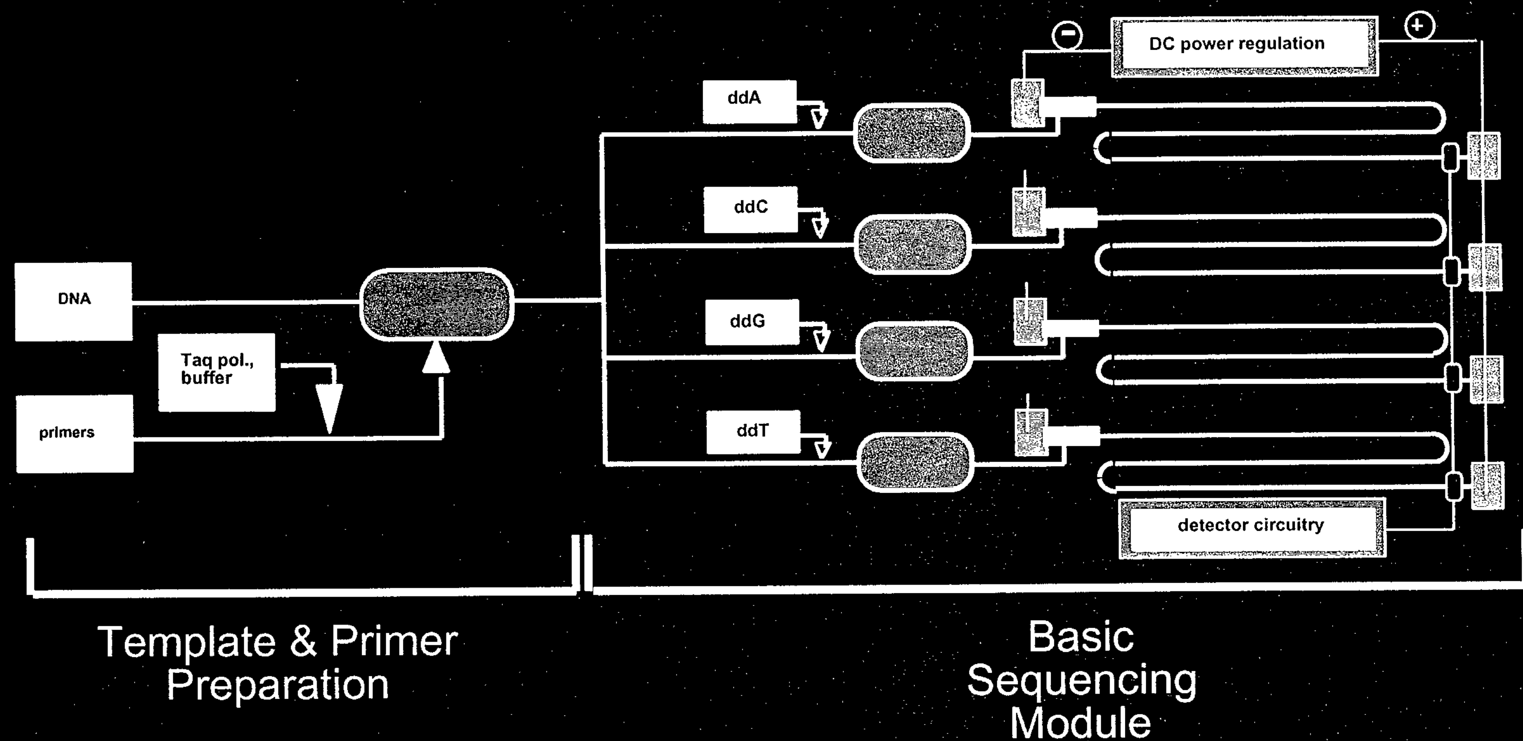
- Separation + detection
- PCR + separation
- Amplification/reaction + labeling + hybridization

Integrated Run

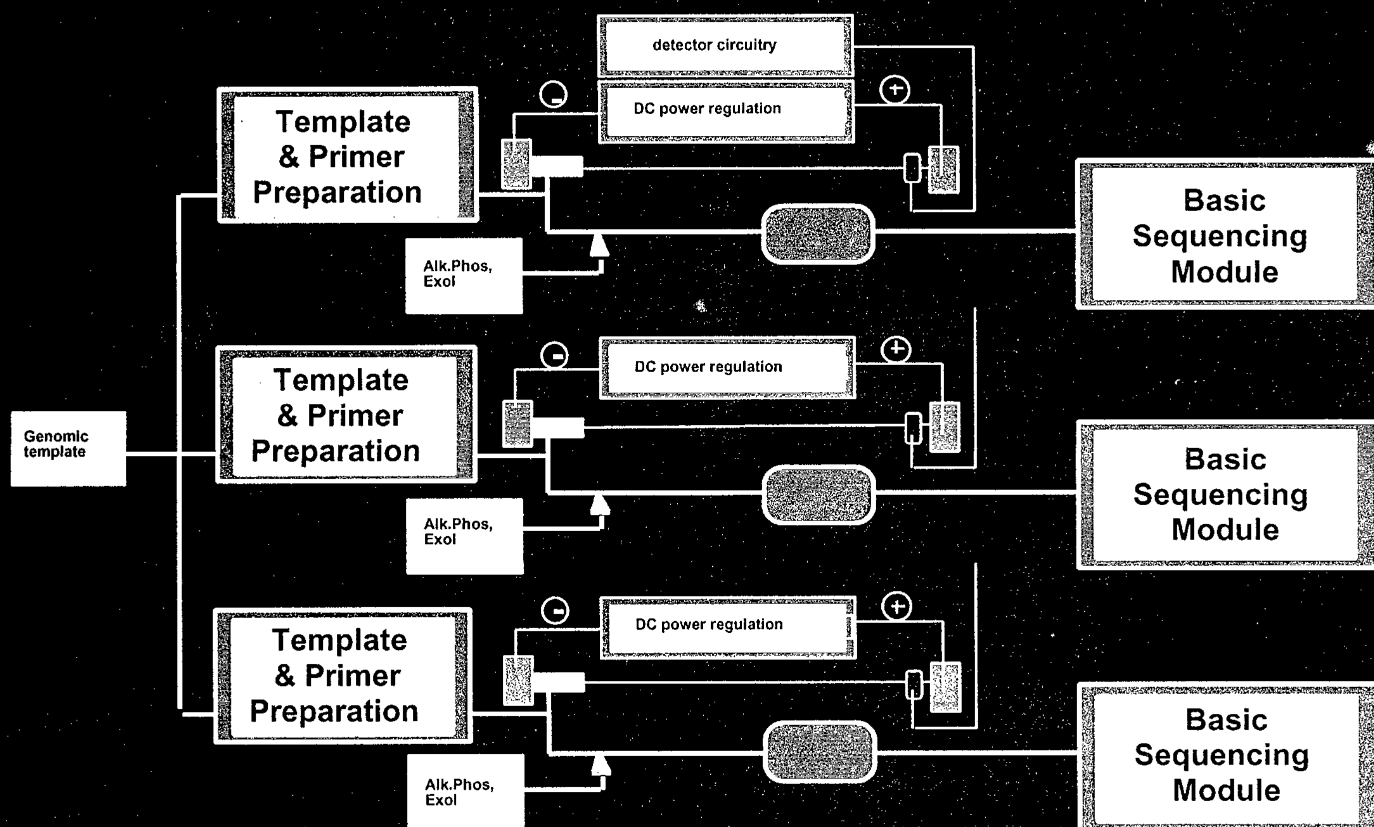


- Injection (µl)
- Meter (120 nl)
- Mix (DNA, Enzymes)
- Amplification (SDA)
- Separation (8 V/cm)
- Detection (on-chip)

Integrated DNA Analysis



Template Characterization



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Current Components

Channels

- Silicon
- Low-stress nitride
- Vapor-deposited polymer
- Injection/cast mold

Fluid motion

- Thermal capillary pumping
- Thermal expansion
- Internal gas generation
- Internal/ external valves

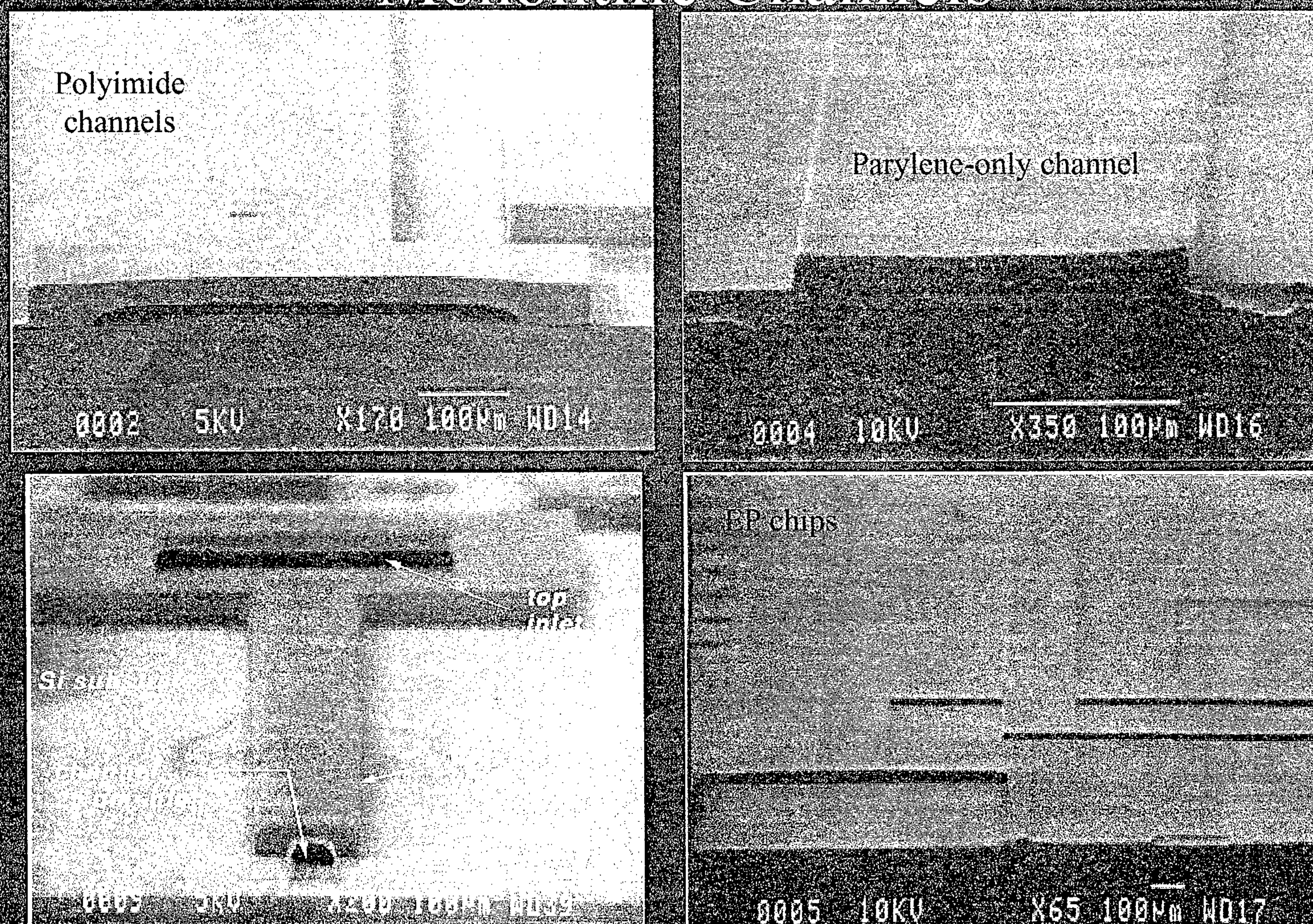
Heaters/Passivation

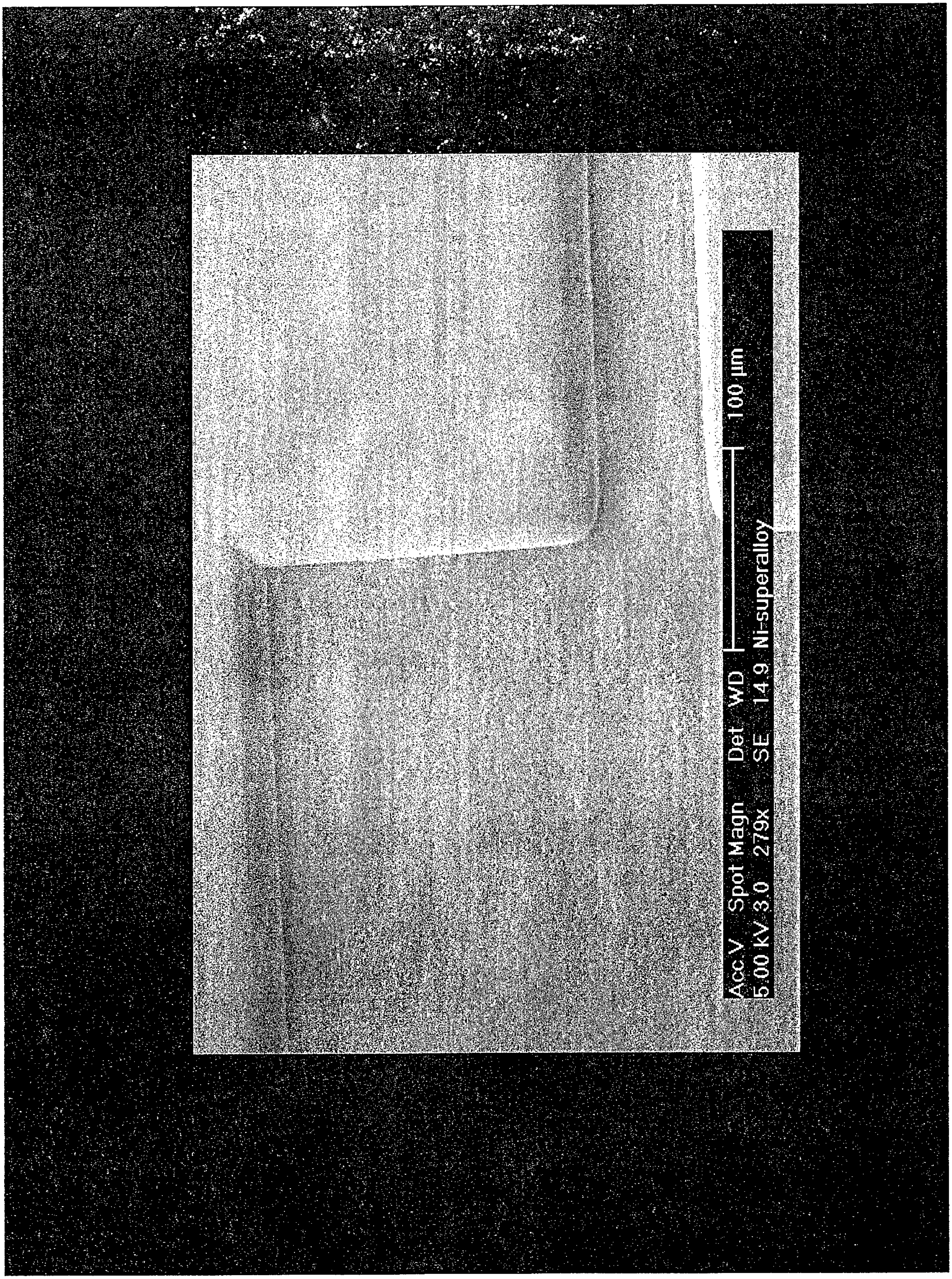
- Doped Si
- Oxide/nitride/oxide
- LTO

Separation/Detection

- Linear matrix
- Poly-Si/Pt electrodes
- Radiation

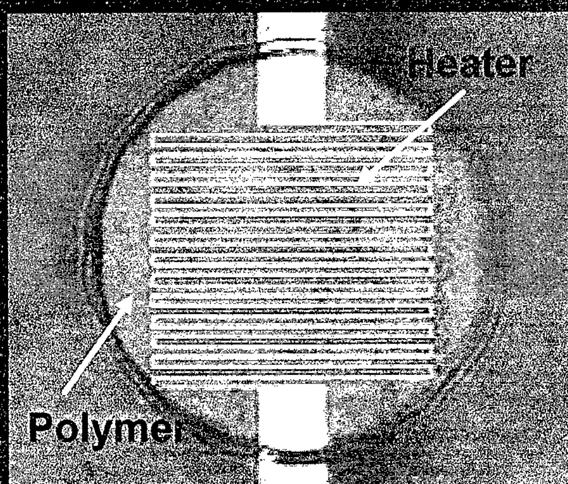
Monolithic Channels

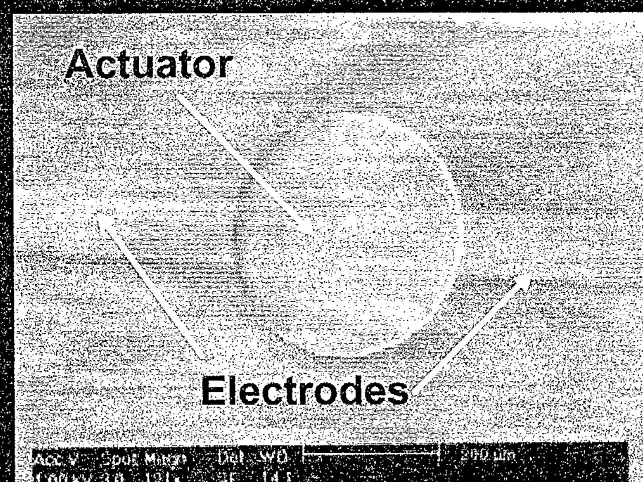



Acc.V Spot Magn Det WD 100 µm
5.00 KV 3.0 279x SE 14.9 Ni-superalloy

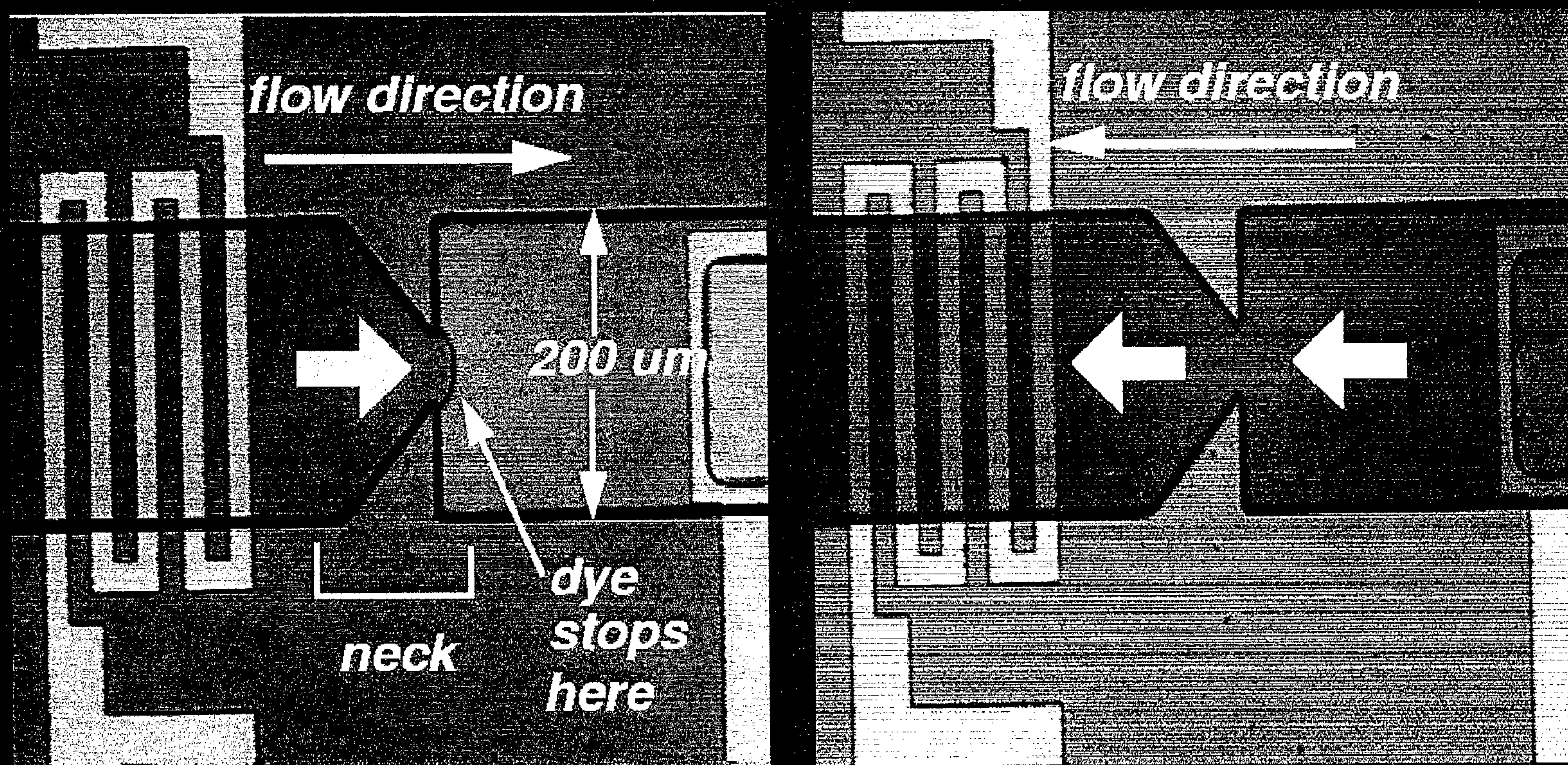
Polymer Actuators

- Patternable polymer matrix
- Thermal expansion
- Large pressure (> 1000 PSI)





Unidirectional flow behavior in horizontal neck valve



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Digest Separation

HaeIII digest of ΦX174 RF DNA

0.5% HEC

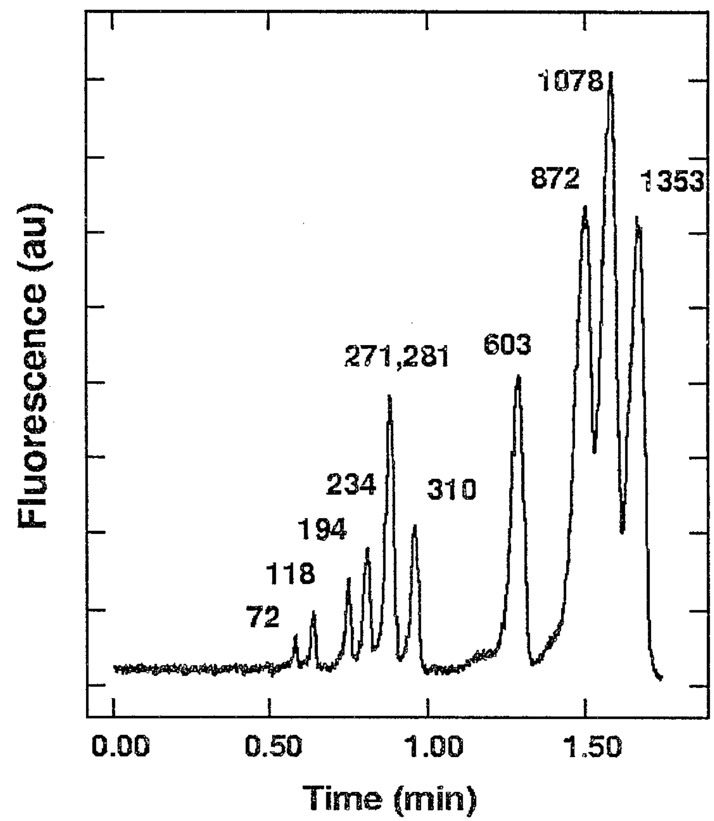
0.1xTBE

110 V/cm

SYBR Green I Dye

1.5 cm Separation length

234 bp ~100000 Theoretical Plates



Conclusions

- Combination of compatible components
- Metering, reaction, separation, detection
- Inexpensive, self-contained, complex systems possible

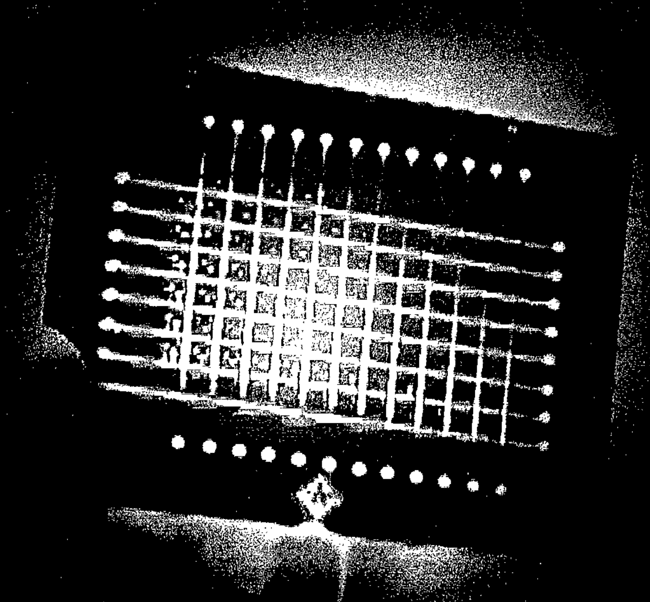
ORCHID

Recent Results of Chemical Synthesis on a Microfluidic Chip

Rolf E. Swenson

Microchemical Systems and Their Applications

June 16-18 1999



ORCHID

Orchid's Mission

Accelerate the commercialization and industrialization of drug discovery through integrated microfluidic, microchemistry, and pharmacogenetics systems

ORCHID

Orchid at a Glance

- Employees: 80
- Facilities:
  - 1 location
  - 32,000 sq ft
- Intellectual Property:
  - >50 issued & allowed patents
  - >140 pending
- Contracts
  - government and corporate

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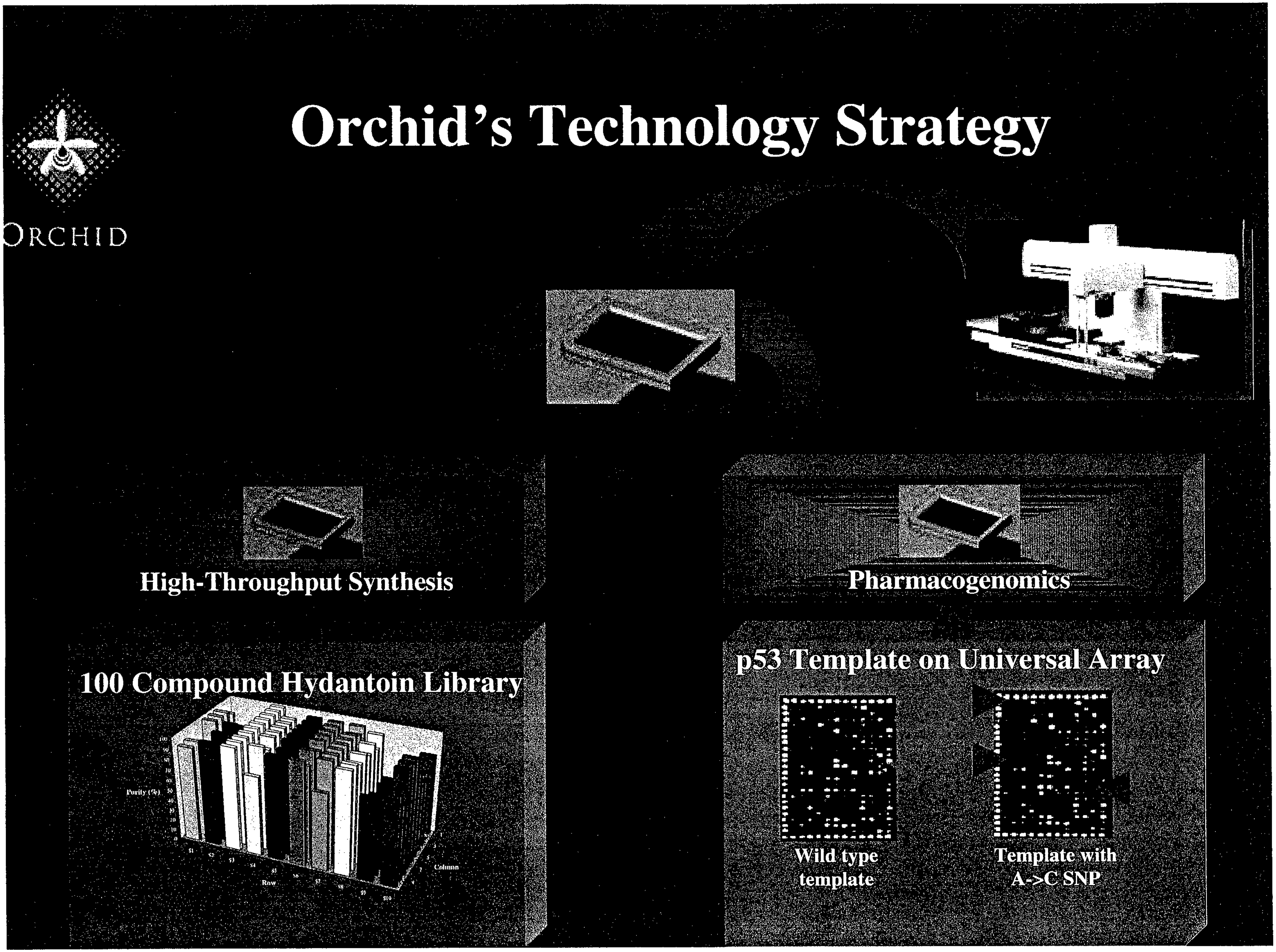

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Orchid's Technology Strategy
High-Throughput Synthesis
Pharmacogenomics
100 Compound Hydantoin Library
Purity (%)
Row
Column
p53 Template on Universal Array
Wild type template
Template with A->C SNP

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ORCHID

Why Microsystems? The Solution for High Volume Processes

- Decreased Cost
- Increased Throughput
- Increased Analytical Sensitivities
- Promotes seamless integration
  - Analytical Chemistry — MassStream™
  - Combinatorial Chemistry → ChemStream™
  - High Throughput Screening / ADMETox
  - Genomics → SNPstream™

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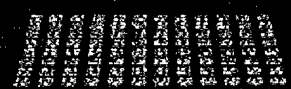
Orchid's Platform Technology

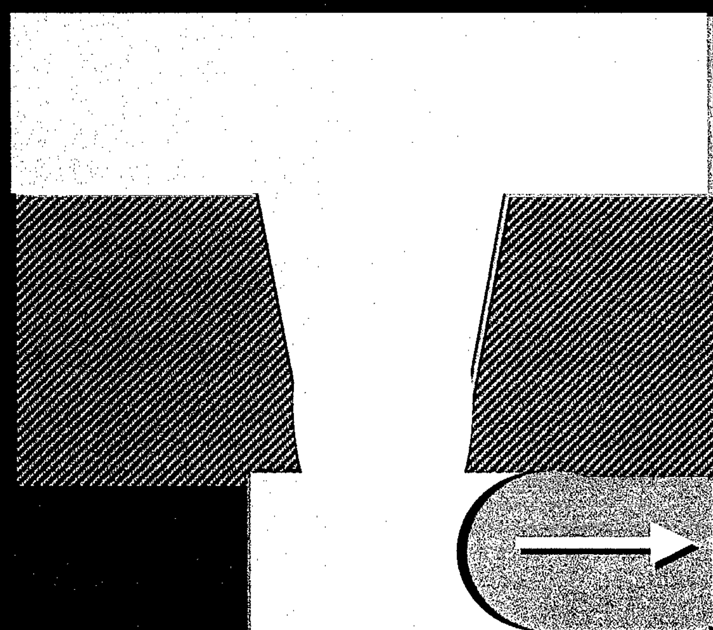


- Parallel Processing
  - Multilayer structures
  - Vertical & Horizontal fluid flow
- Full materials compatibility
- Precision Microfluidics
  - On-chip pumps & valves

ORCHID

Precision Fluidic Delivery: Capillary Break Mechanism

Apply Pressure



Column Feed

Capillary Hold

Capillary Break

Fluid Flow

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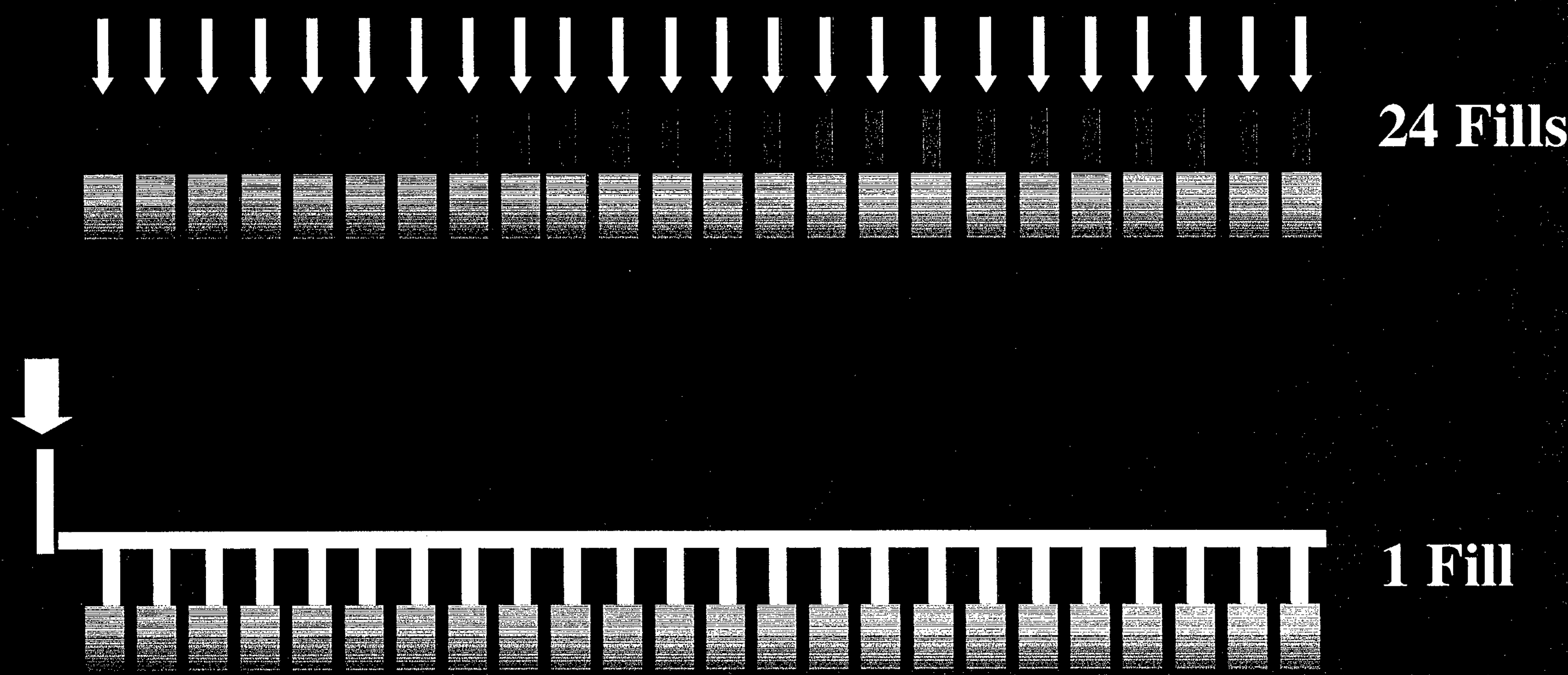
24 Reactor Filling: Serial vs Parallel



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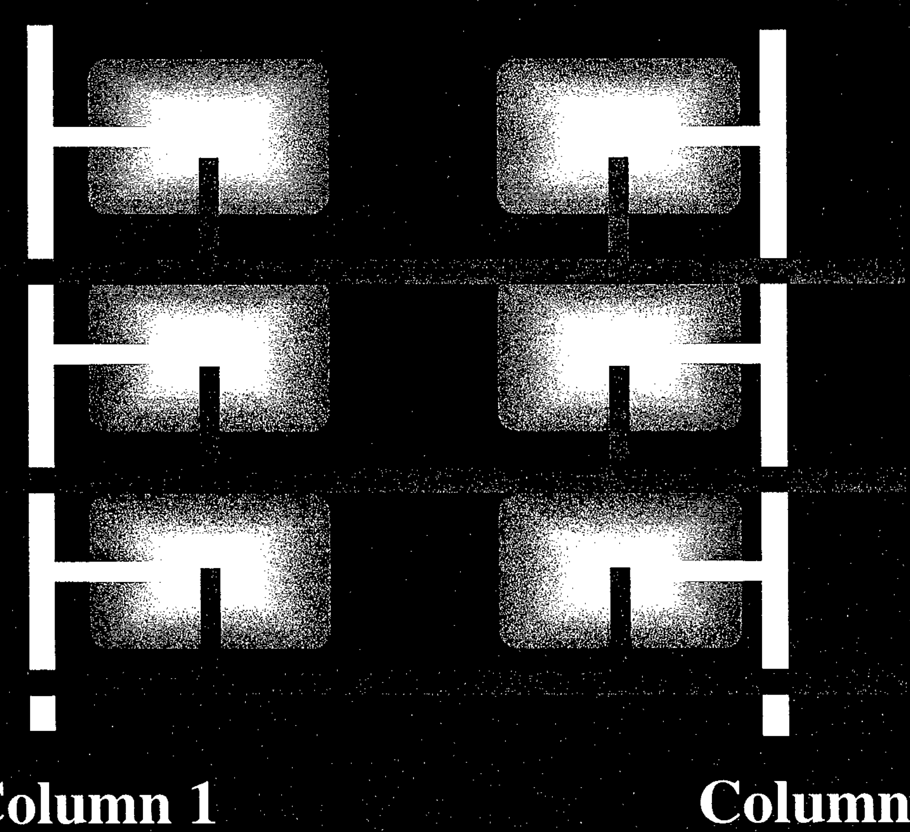
Row & Column Fluidic Distribution



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384 Chip: 24 Column Fills

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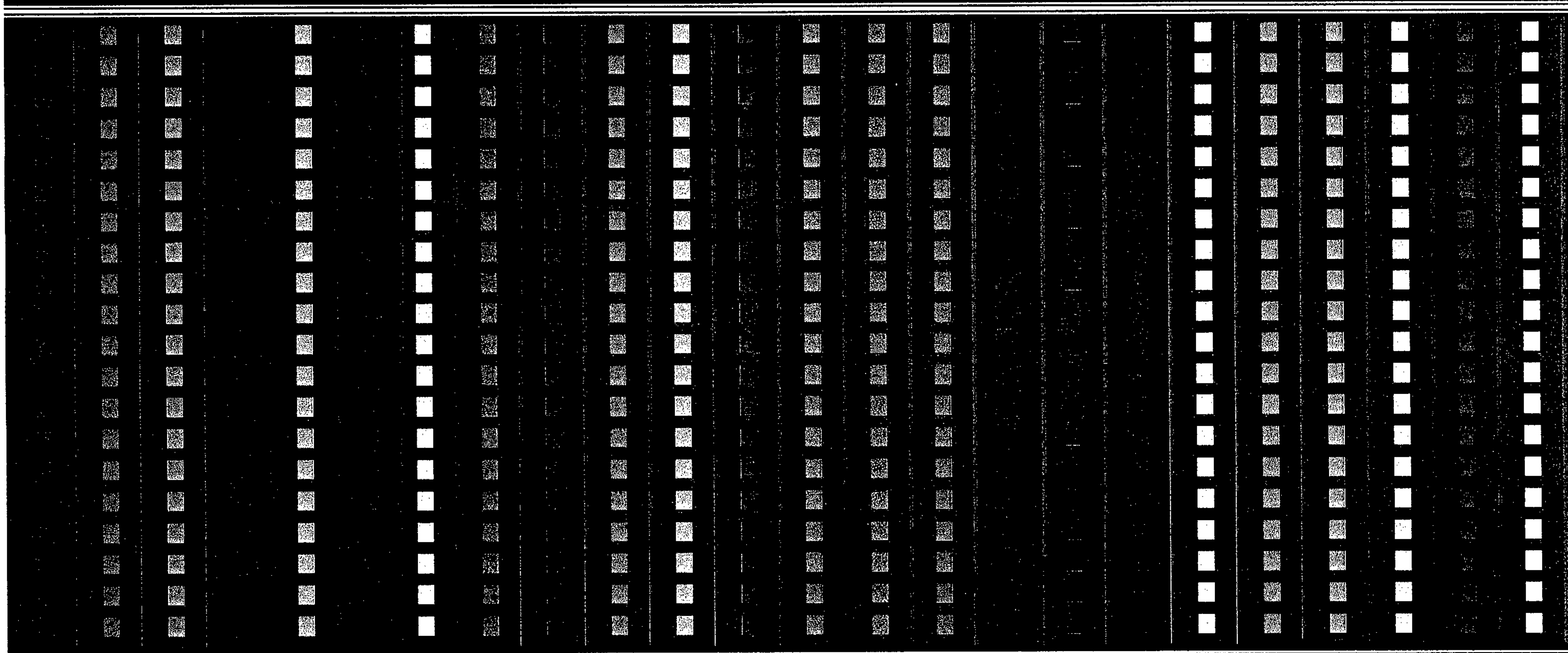

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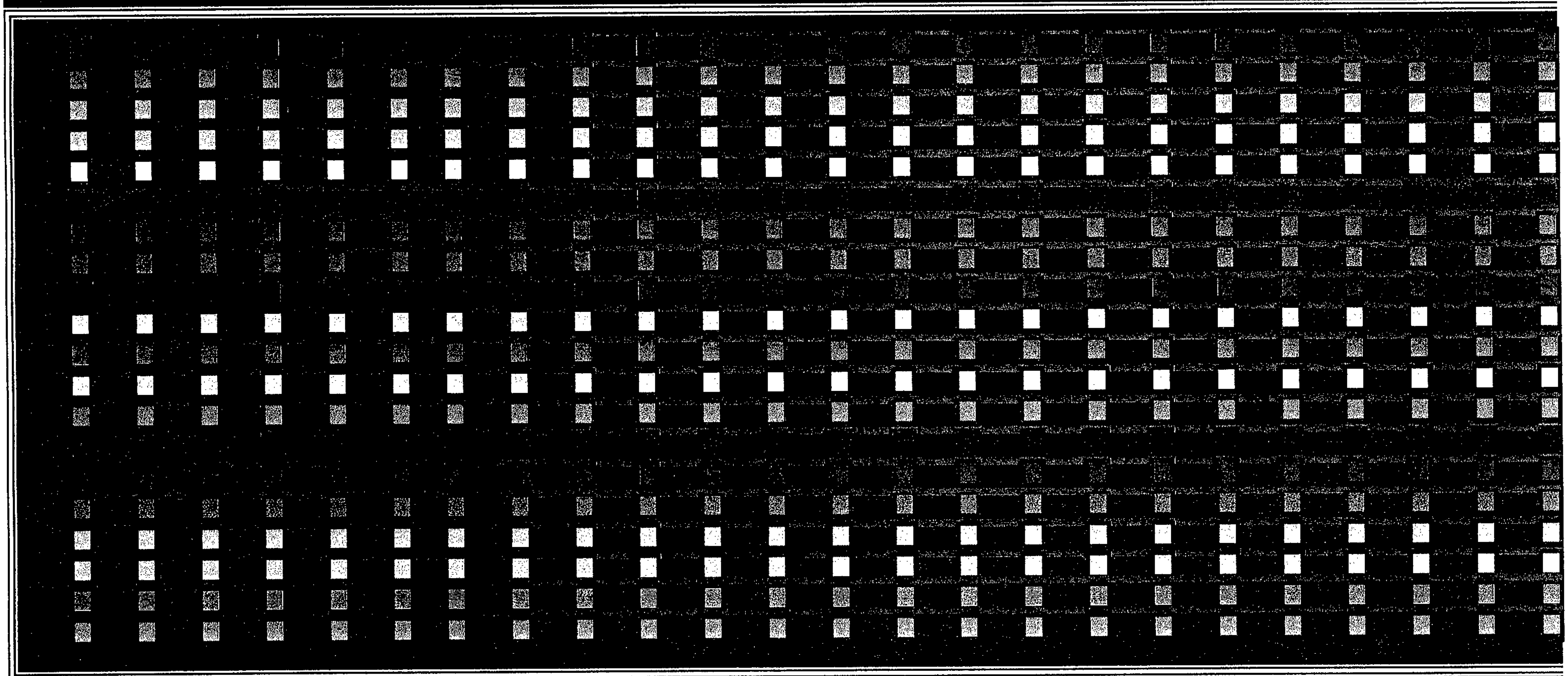
384 Chip: 16 Row Fills



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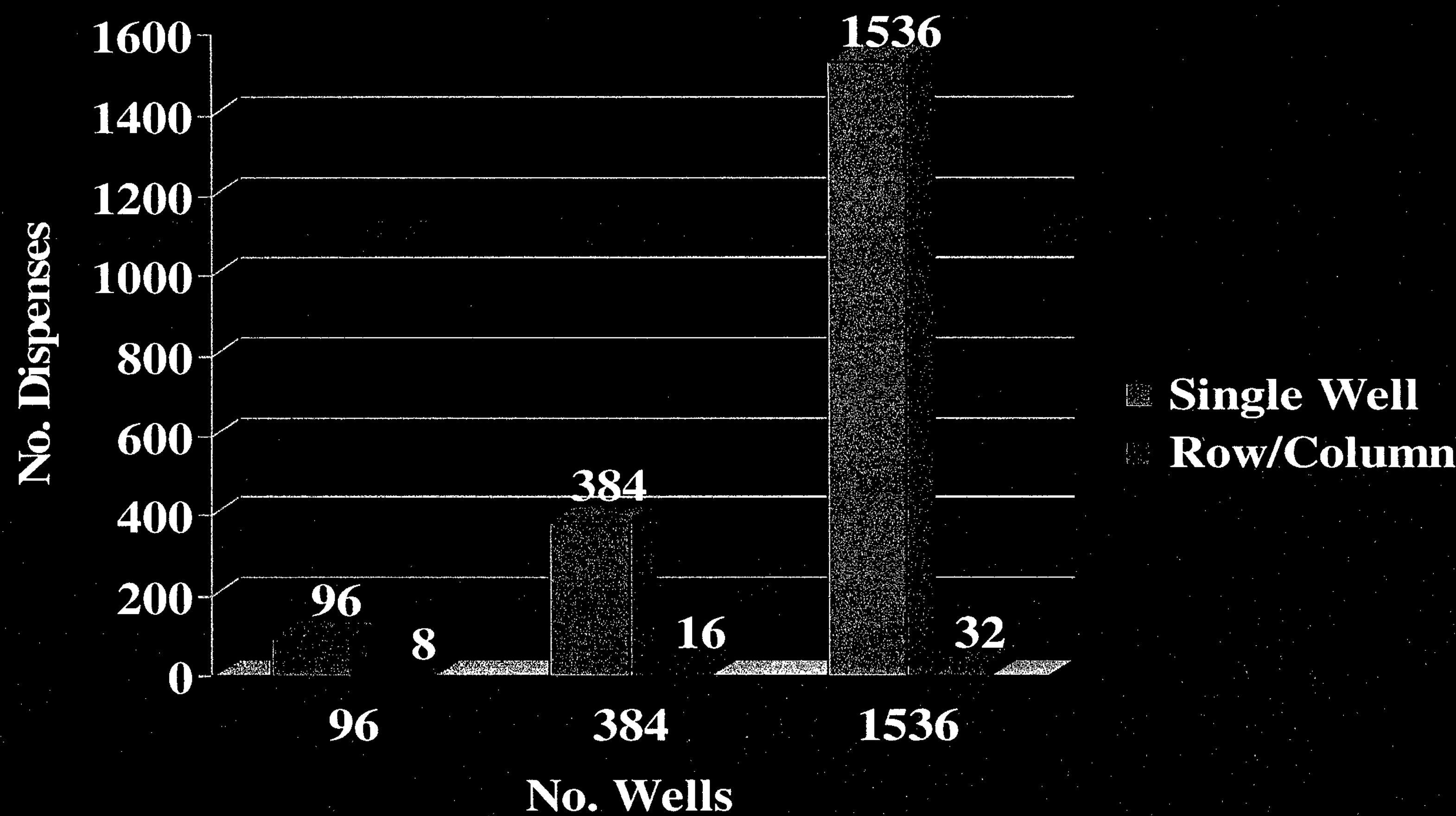
Benefit of Dispensing Method



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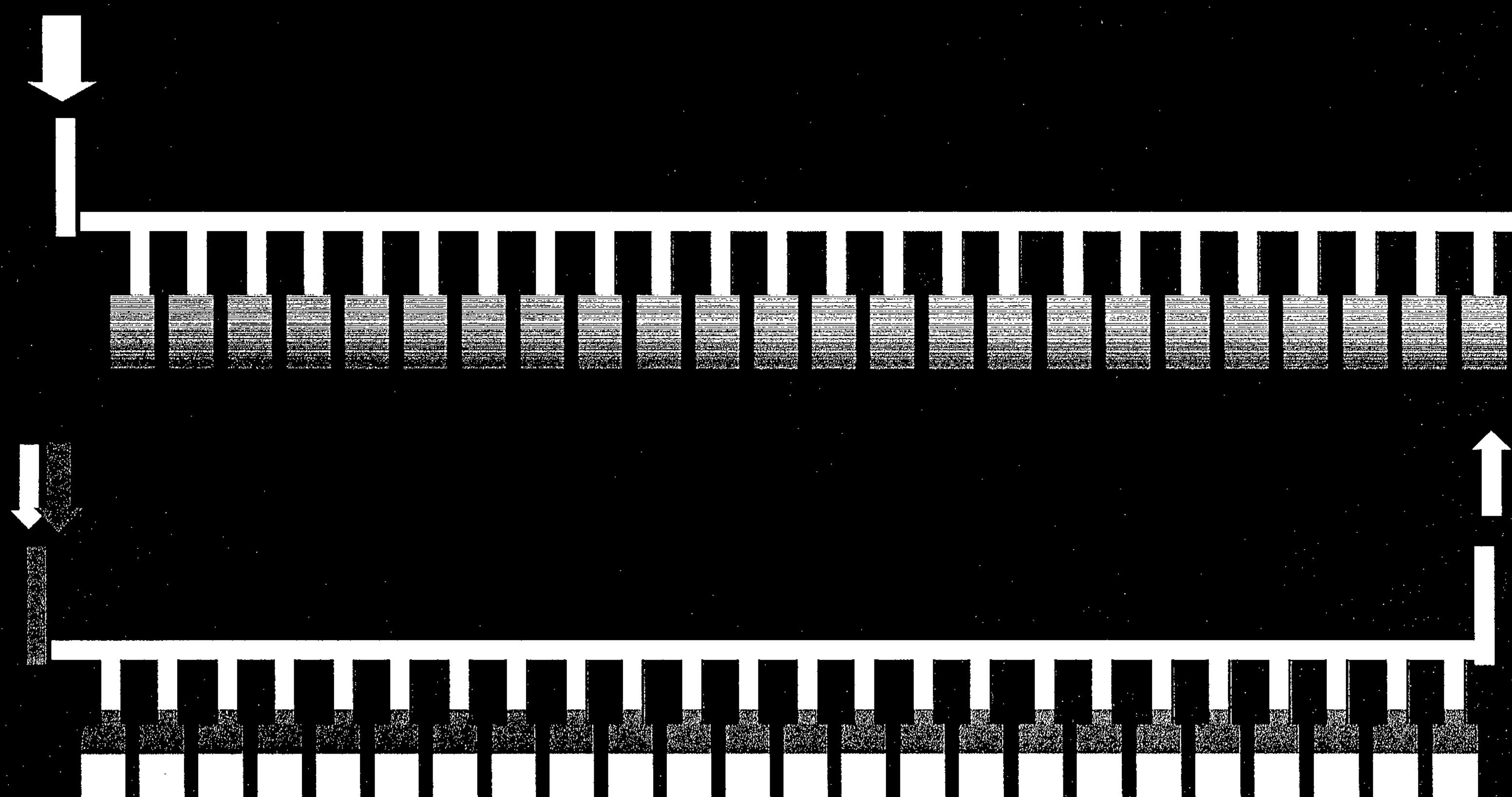
Pressure Filling & Vacuum Draining



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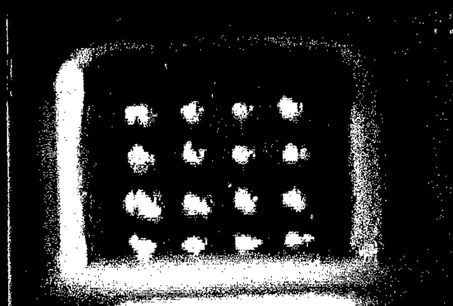
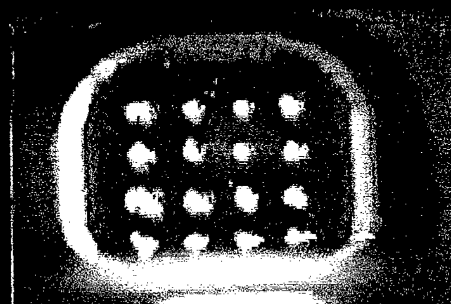
Partial Well Filling

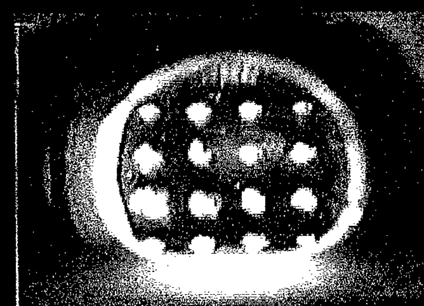


Empty

0 nl

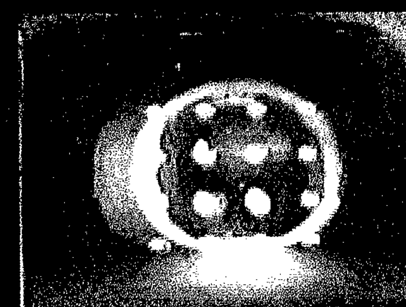


100 nl



8 pulses

200 nl

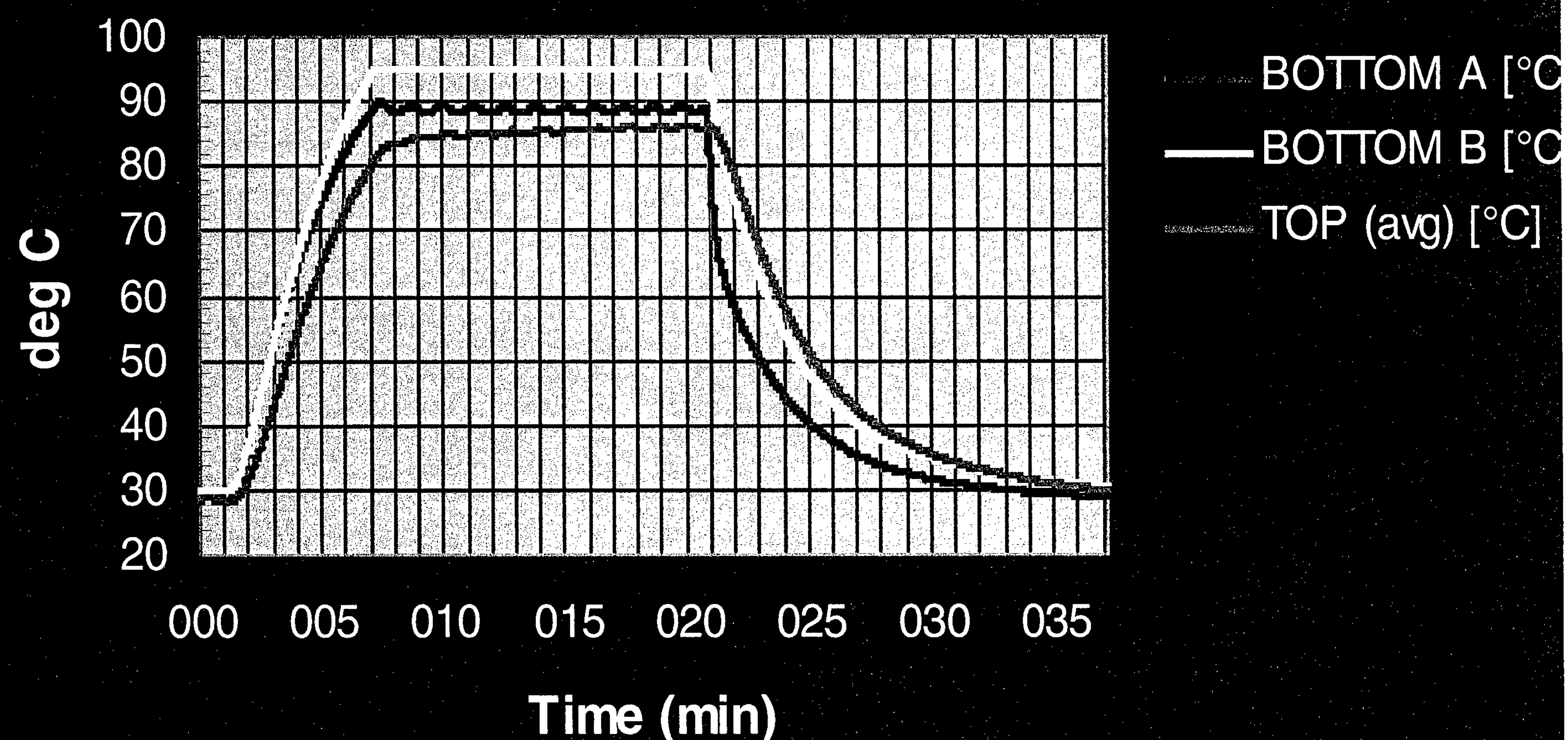


12 pulses

300 nl

Heating to 100°C on the 144 Station

Foil Heater 100C w/ Active Cooling



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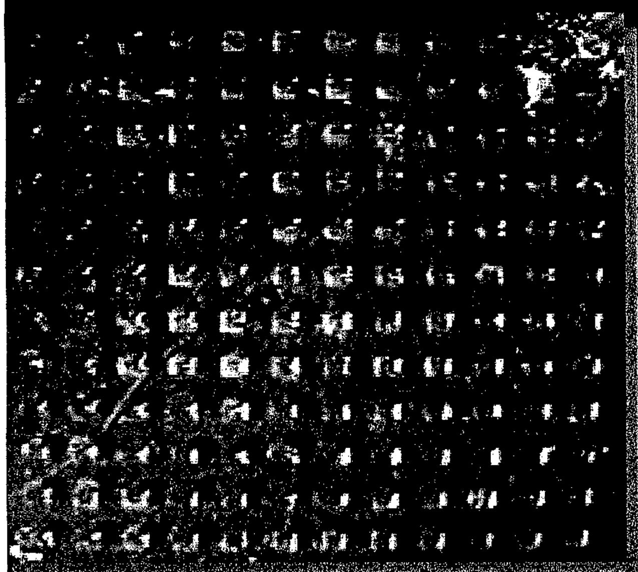
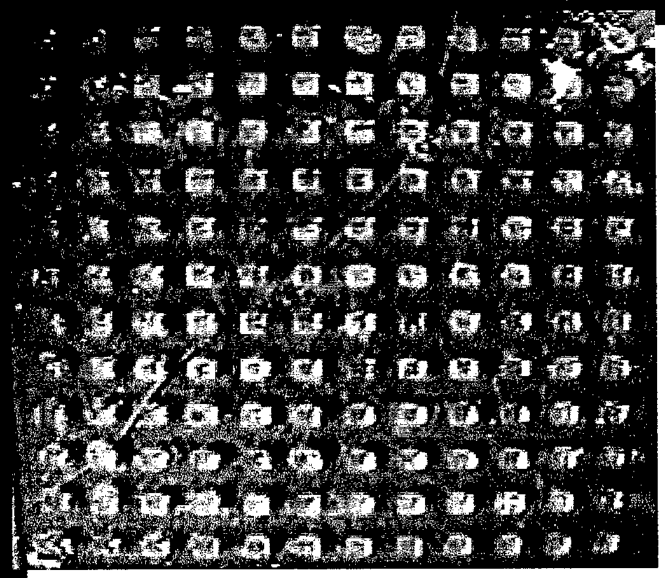
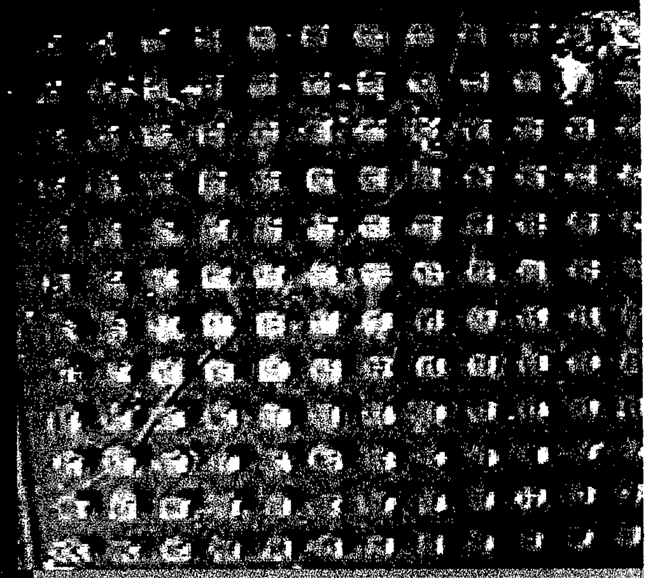
Temperature Control at 100°C with Liquid Crystal Detection



T = 0 min
Ambient



T = 5 min
Yellow = 98°C



T = 10 min
Blue = 102°C

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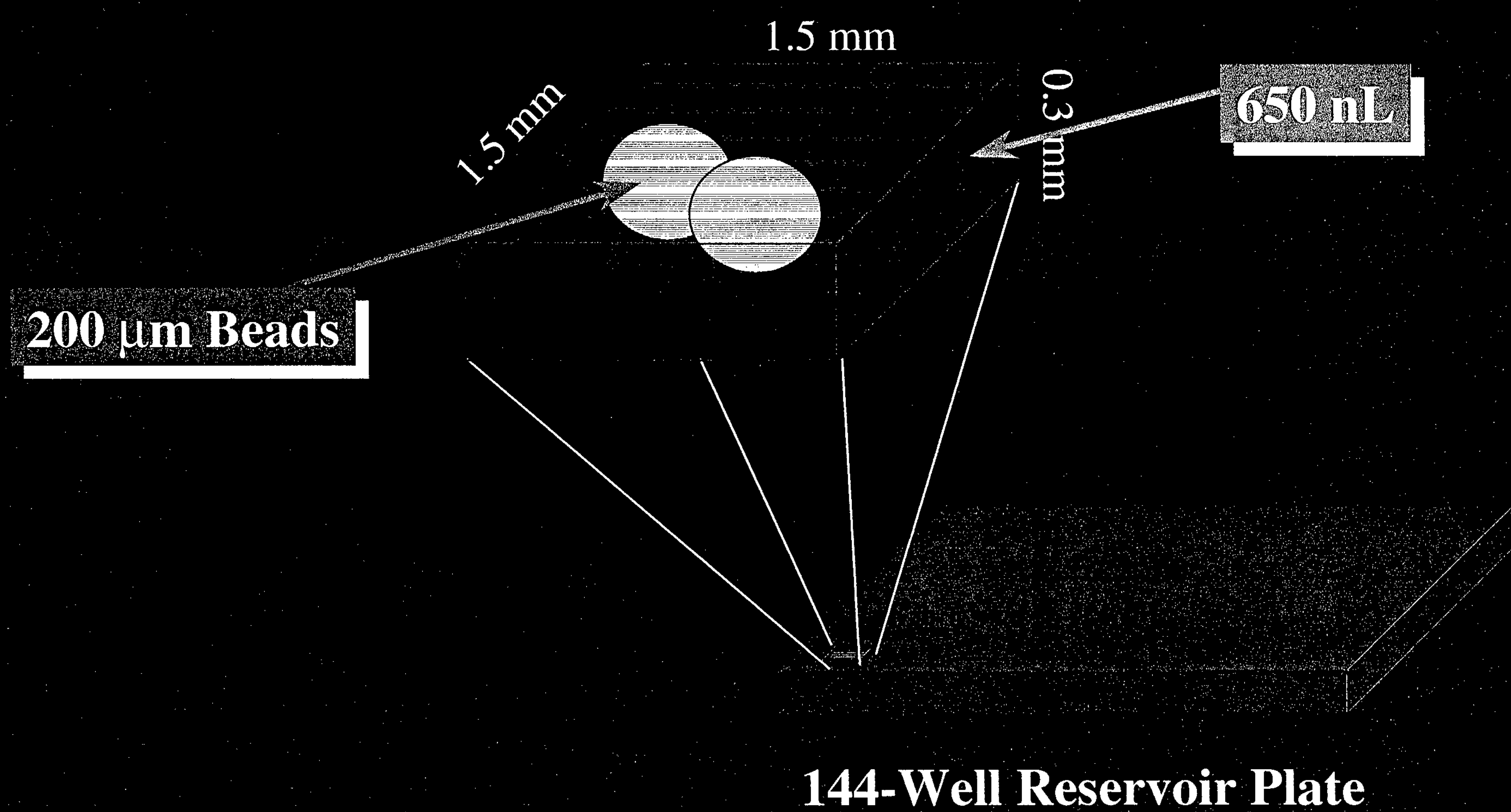
Current Reaction Well Design



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The Fluidics of a Single Reactor

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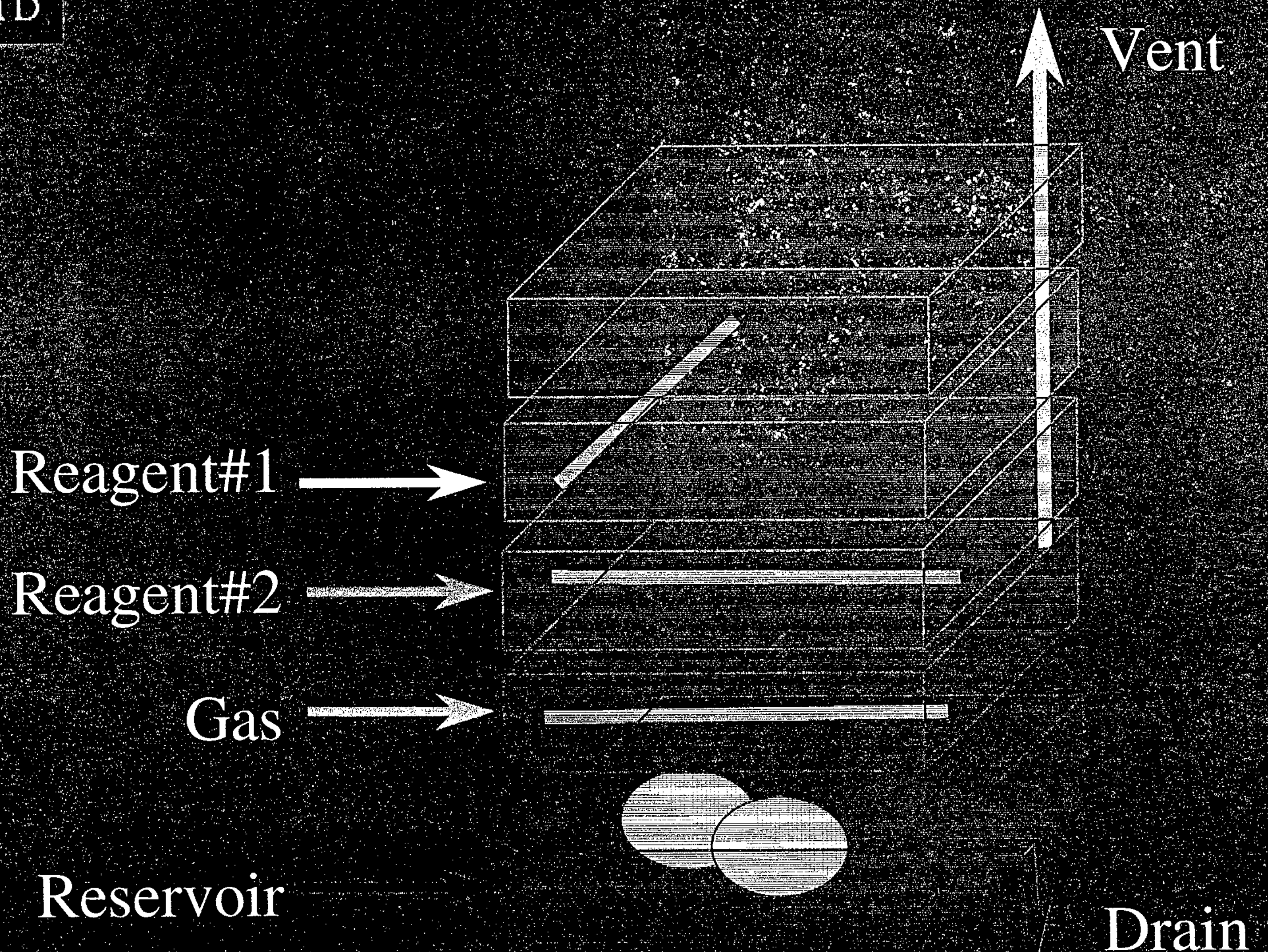

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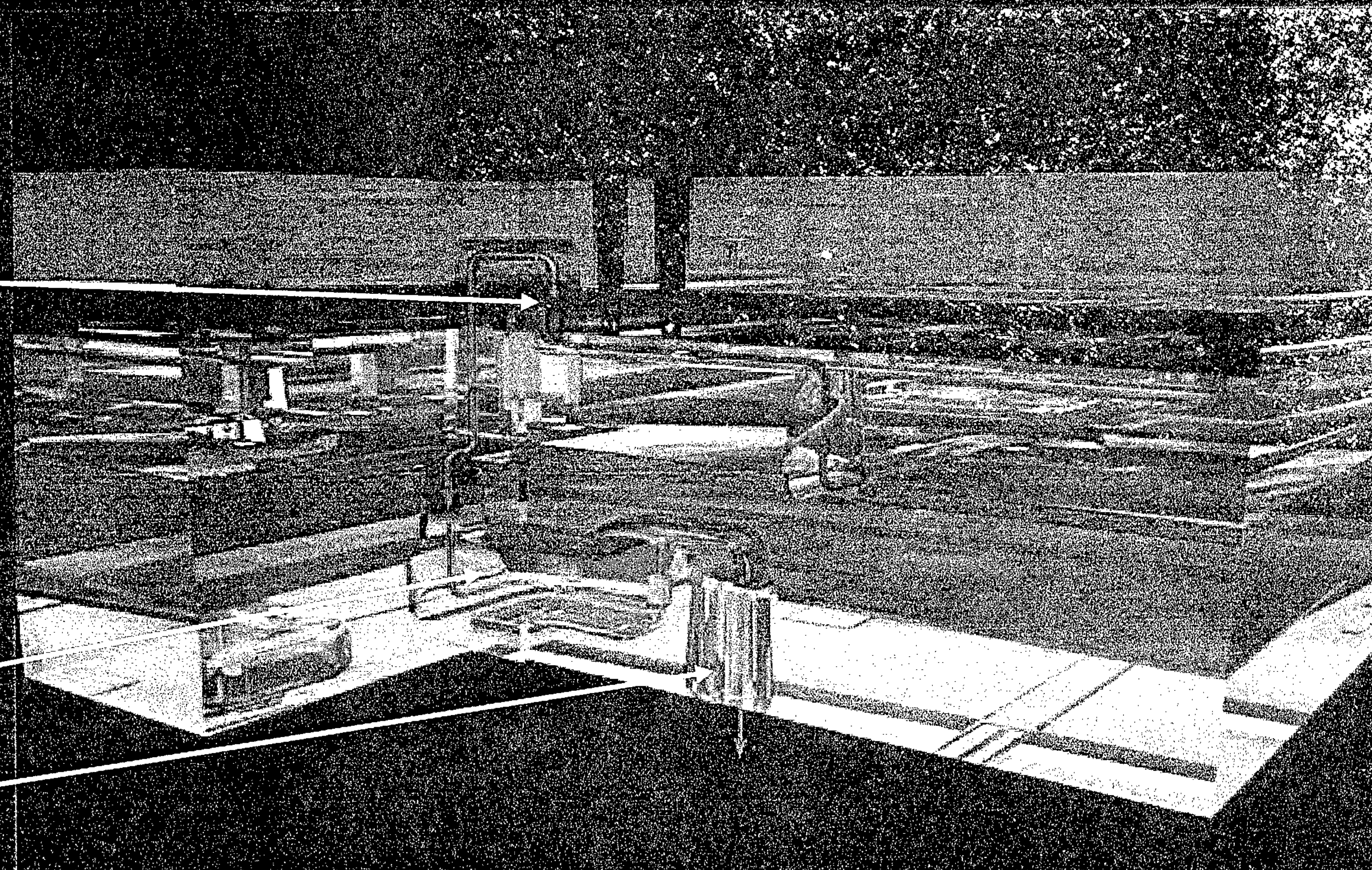
Multilayer Synthesis Chip



Capillary Valve

Reaction Well

Waste Exit

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100 Well Chemtel™ Chip

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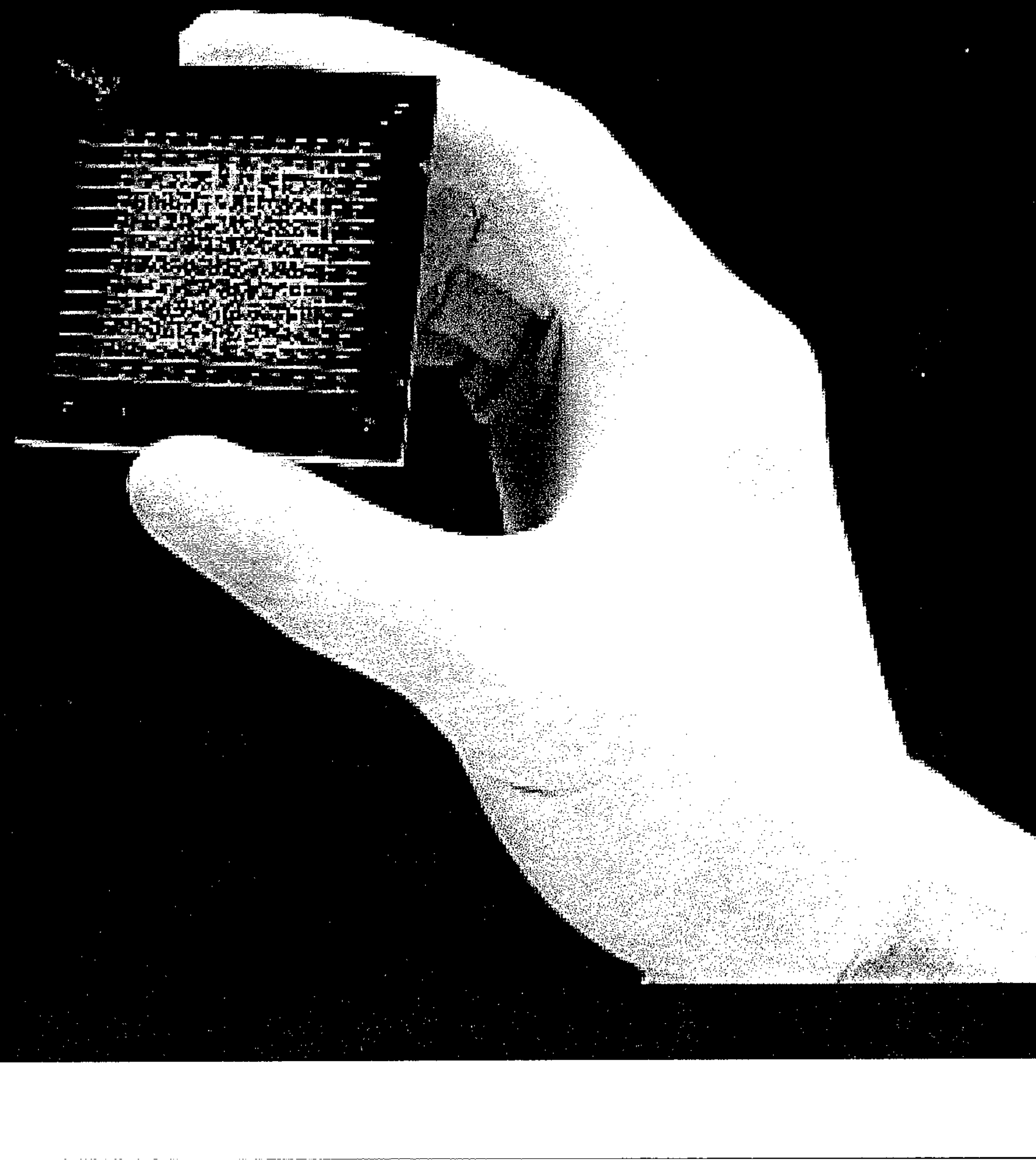

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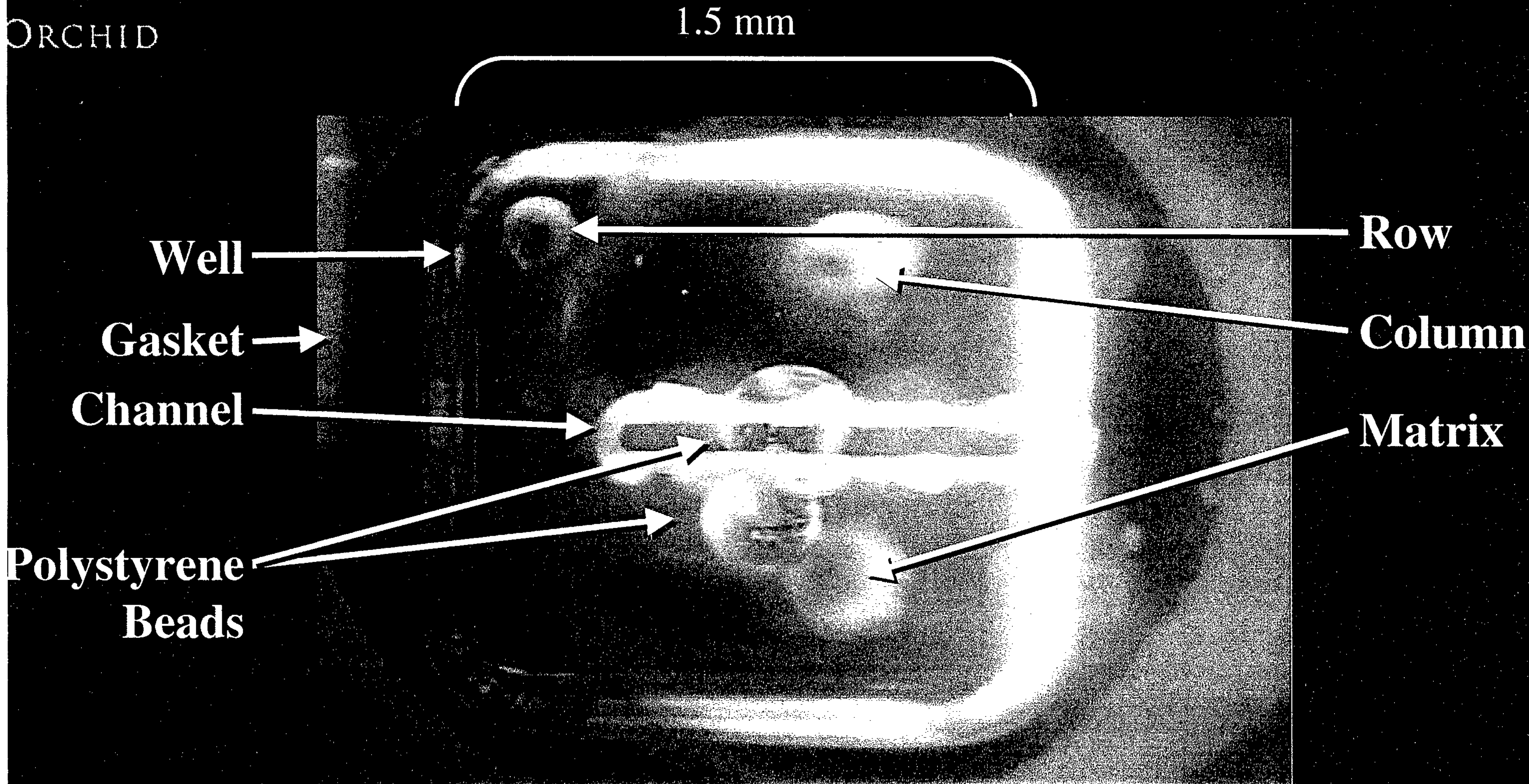
Reaction Well Detail



Volume = 100-800 nL

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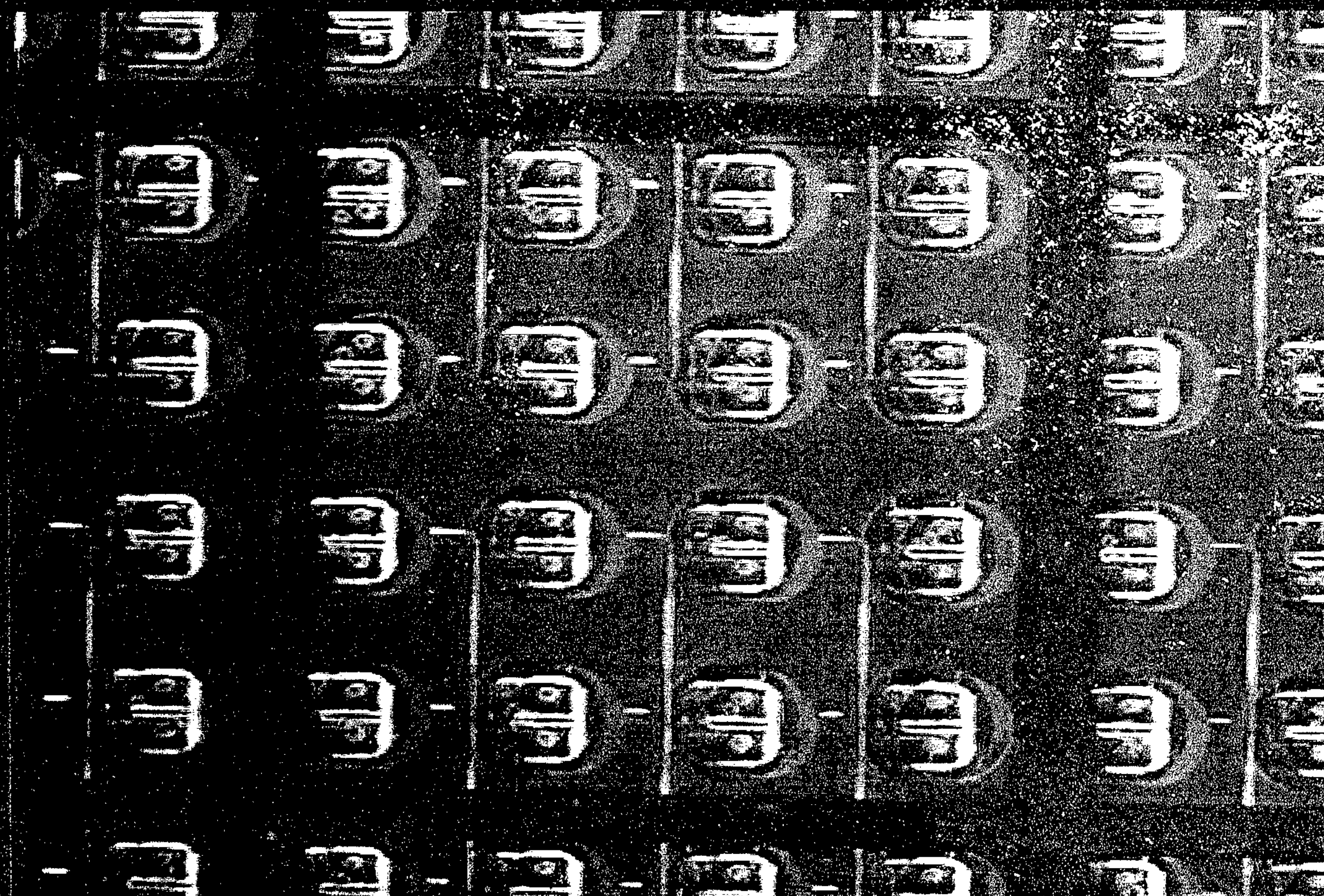
Reaction Wells During Operation



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Visualization within Chemtel™ Chip

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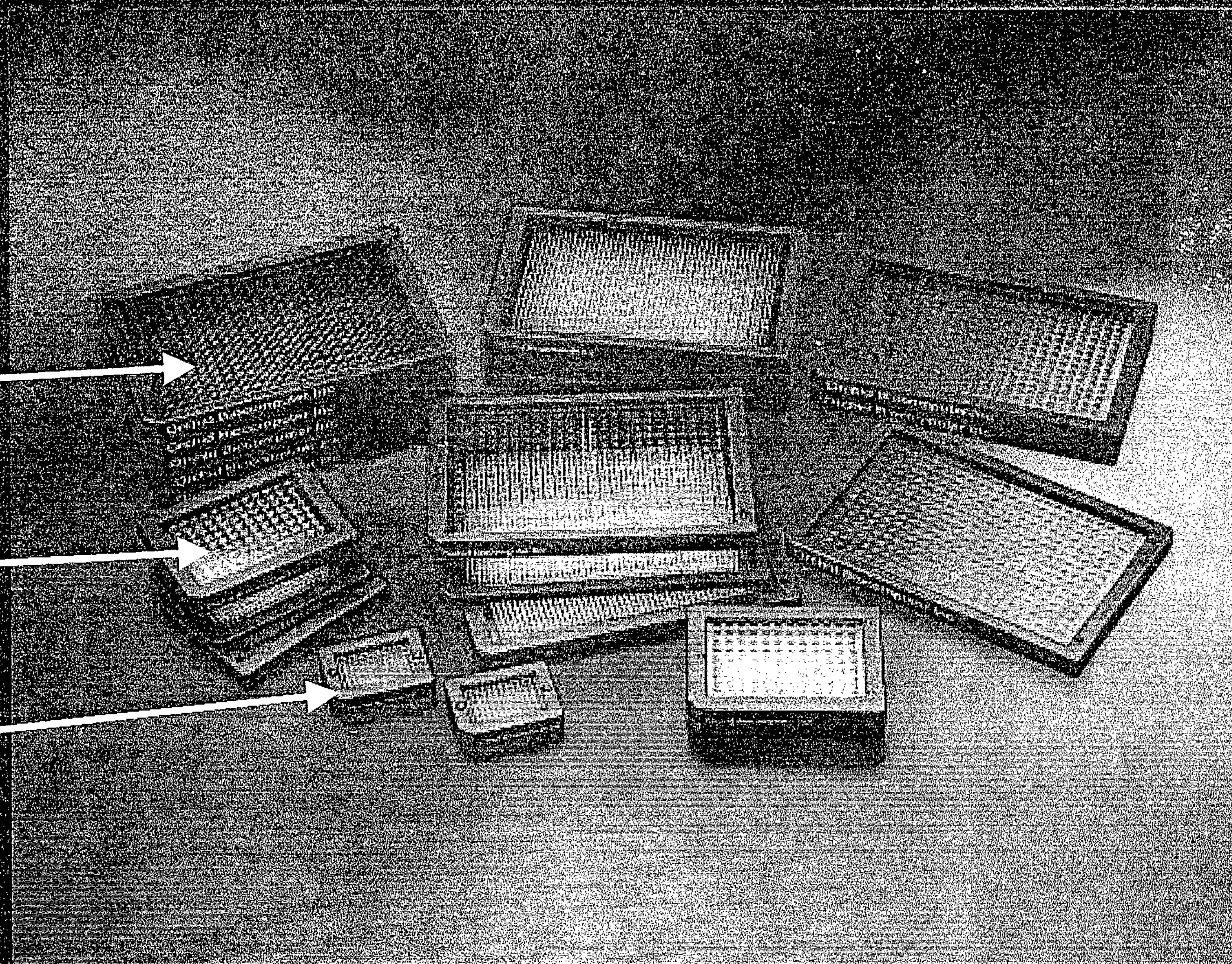
Orchid's Family of Chips

1536 Chip

384 Chip

96 Chip



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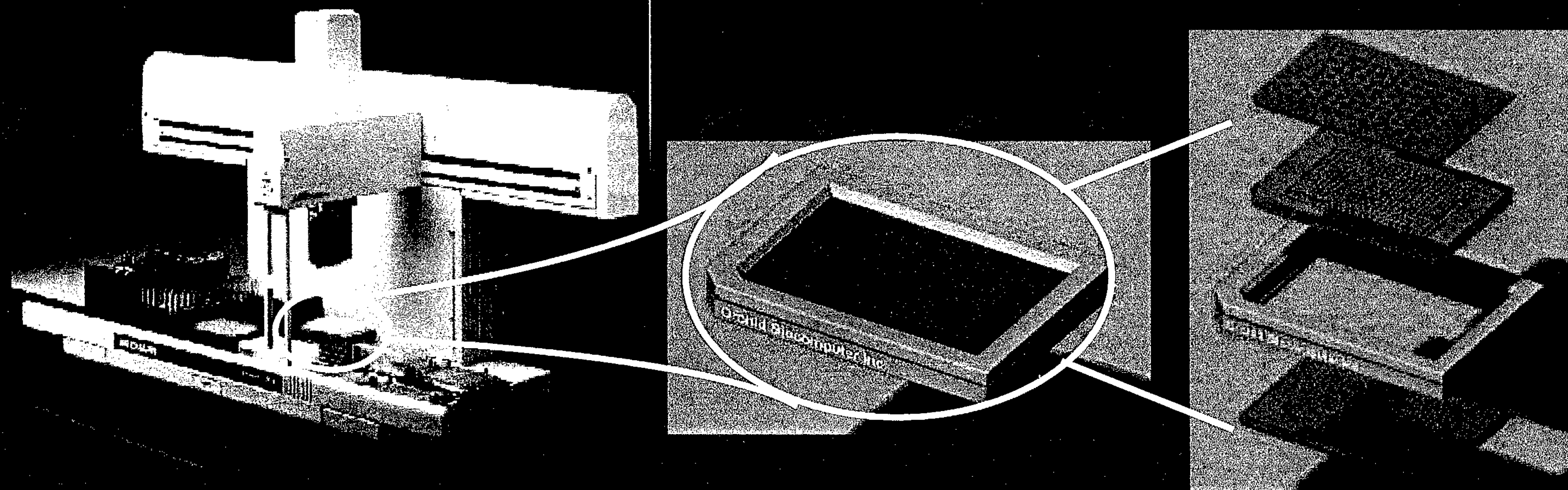
Chip Automation for Applications



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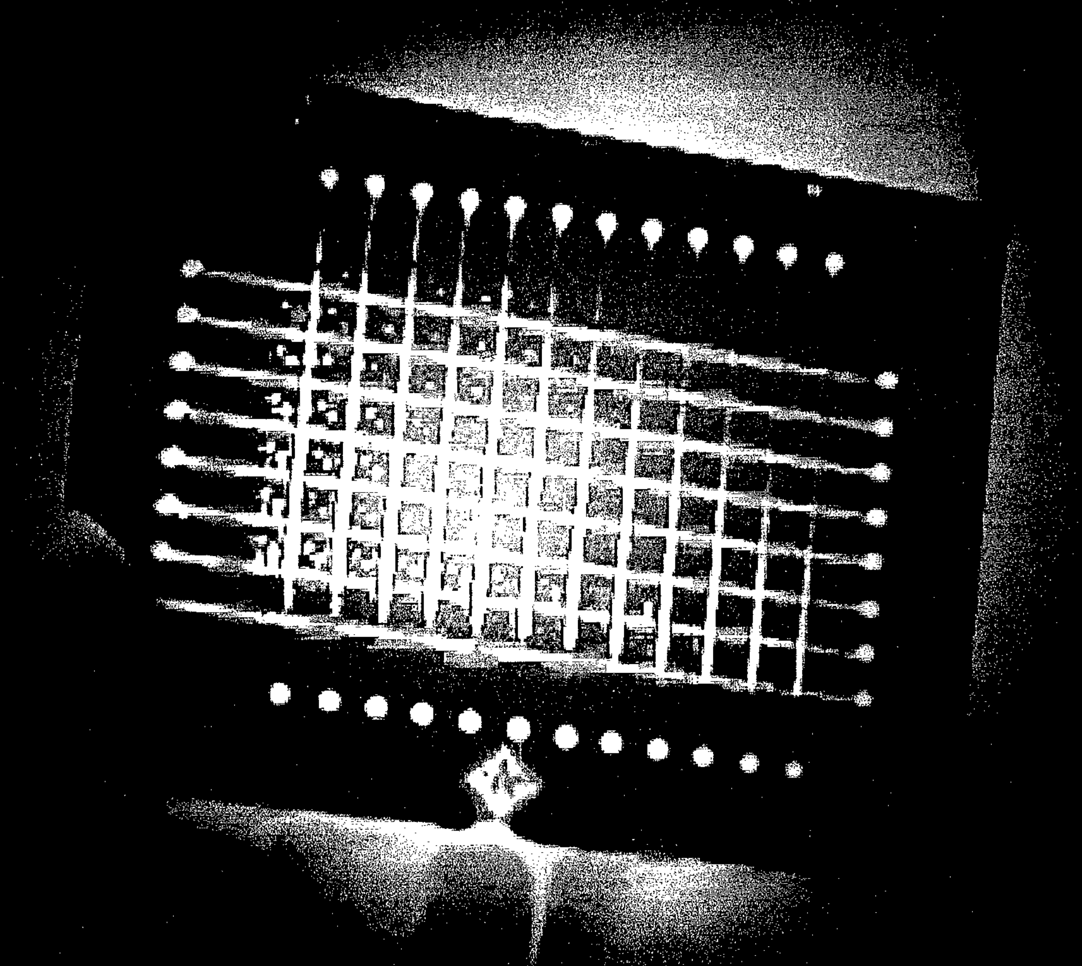
96 Well Chemtel™ Chip



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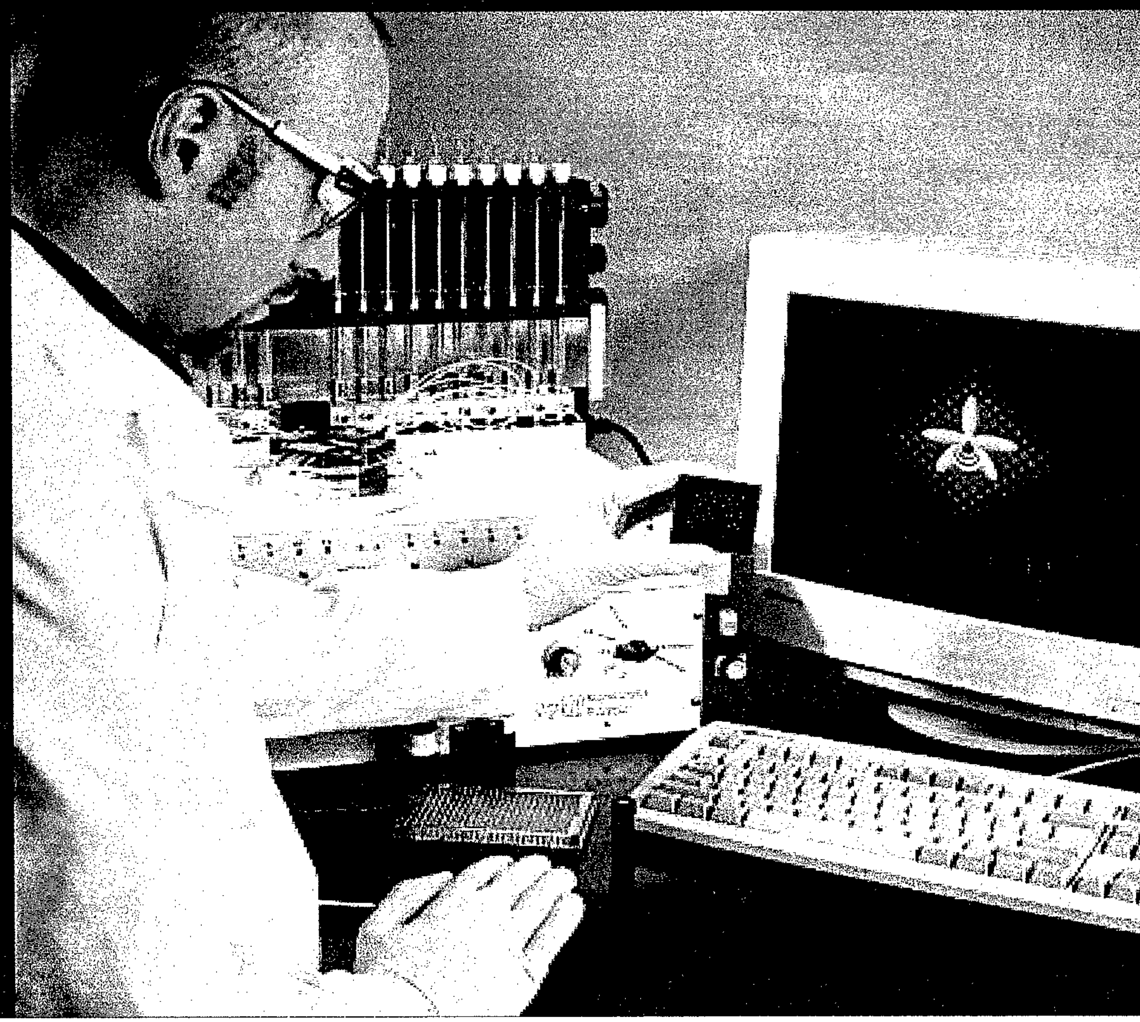
Chemtel™ Chip & ChemStream™ Processor



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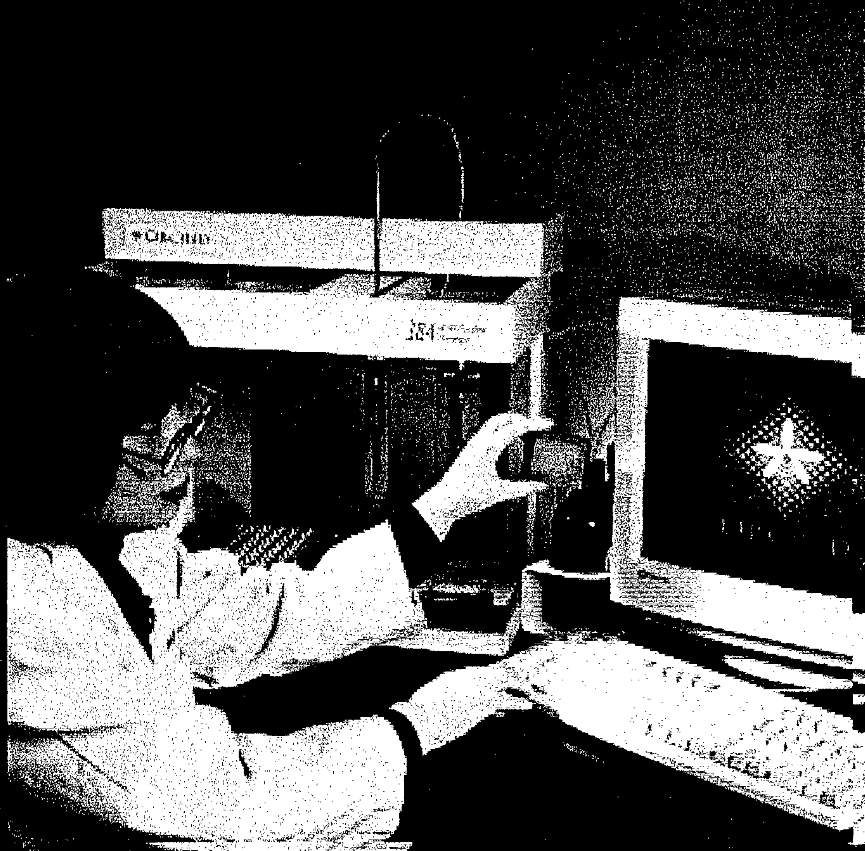
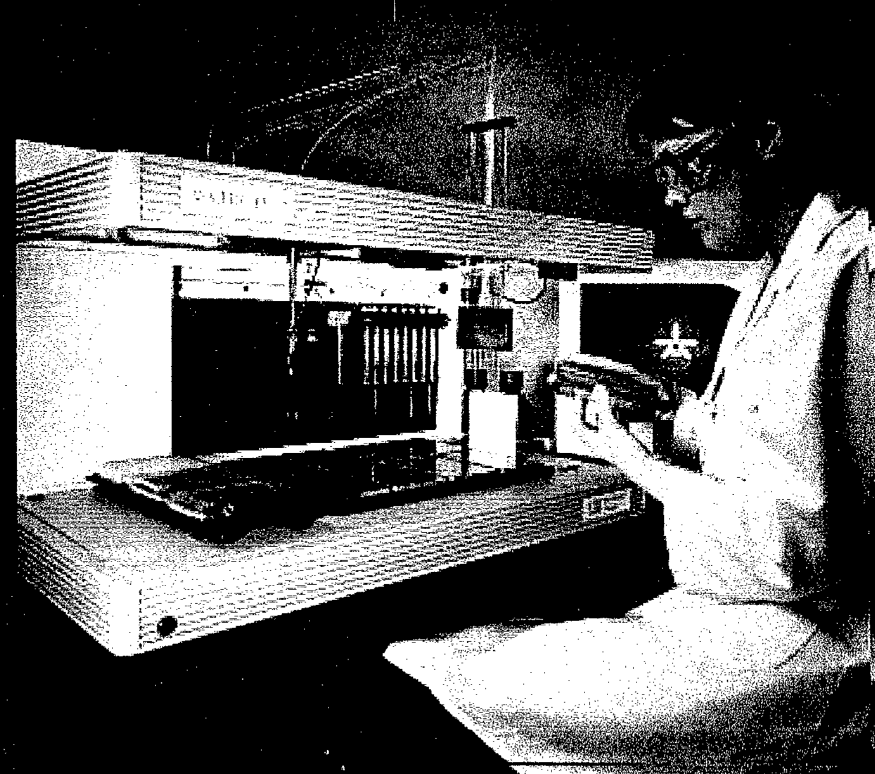
ChemStream™ Processors



384 ChemStream



12K ChemStream

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Demonstrated Reaction Conditions

- Solid Phase Chemistry
- New Solution Phase Chemistry
- New Temperature Control (RT to 100°C)
- Hazardous Reaction Conditions (TFA)
- Sensitive Reaction Conditions (RNCOs)
- New Purification by Resin Capture

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Demonstrated Benefits of Chip Synthesis

- Controlled reaction environment
- Rapid Mass & Heat Transfer
- Chemical compatibility
  - Glass construction
  - Non-mechanical valves
- Cost Savings on Reagents
- Increased Safety
- Enhanced reaction kinetics
- Cleaner products - less side reactions

Potential Benefits
Novel Compounds
Purer Products

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Utility of Microchemistry & Analysis

- Reaction Optimization
  - SPOS Development
  - Process Chemistry Route Scouting
  - Hazardous Reaction Conditions
- Lead Optimization
  - Quantitative HTS Knowledge
- Chemical Manufacturing

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Current Limitations of Chip Synthesis

- Requires solutions or very fine suspensions
- Reagents need to be compatible with silicon valves
  - i.e. not KOH at 50°C
- Not demonstrated with high pressure reactions

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SPOS Product Yields in Chemtel^{TM} Chip

No. Beads	Theory nmol	Theory ug*	No. Assays 96 well	No. Assays 1536 well
2	20	10	[illegible]	200
4	40	20	40	400
8	80	40	80	800

* Theoretical yield of ug based on MW = 500 g/mol

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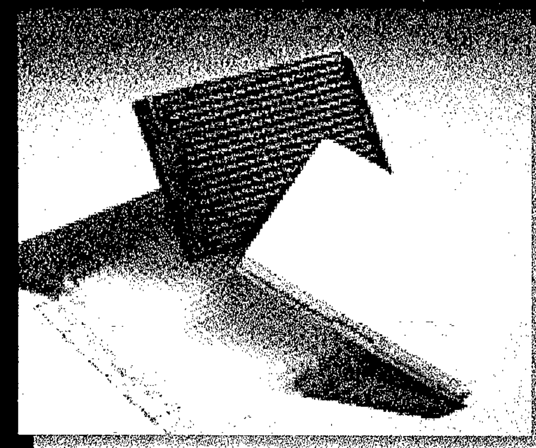
Solution Phase Product Yields in Chemtel™ Chip



Soln Conc (M)	Theory nmol	Theory ug*	No. Assays 96 well	No. Assays 1536 well
0.1	65	33		650
0.5	325	163	325	3250
1.0	650	330	650	6500

* Theoretical yield of ug based on MW = 500 g/mol

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DNA Synthesis Product Yields

	Chemtel Chip	ABI Synthesizer
Minimum Qty (nmol)	1	200
Cost		
Base ($)	$0.01	$1.03
25mer ($)	$0.24	$25.68
10,000 primers	$2,445	$256,750
No. Assays		
96 well	100	20,000
384 well	400	80,000
1536 well*	7,143	1,428,571

* 16 spots per well of 96 well plate

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Solvents Used in Chemtel™ Chip

- TFA
- DMF
- THF
- Chloroform
- Methanol
- NMP
- Chromerge
  - (Sulfuric/Chromic Acid for cleaning)

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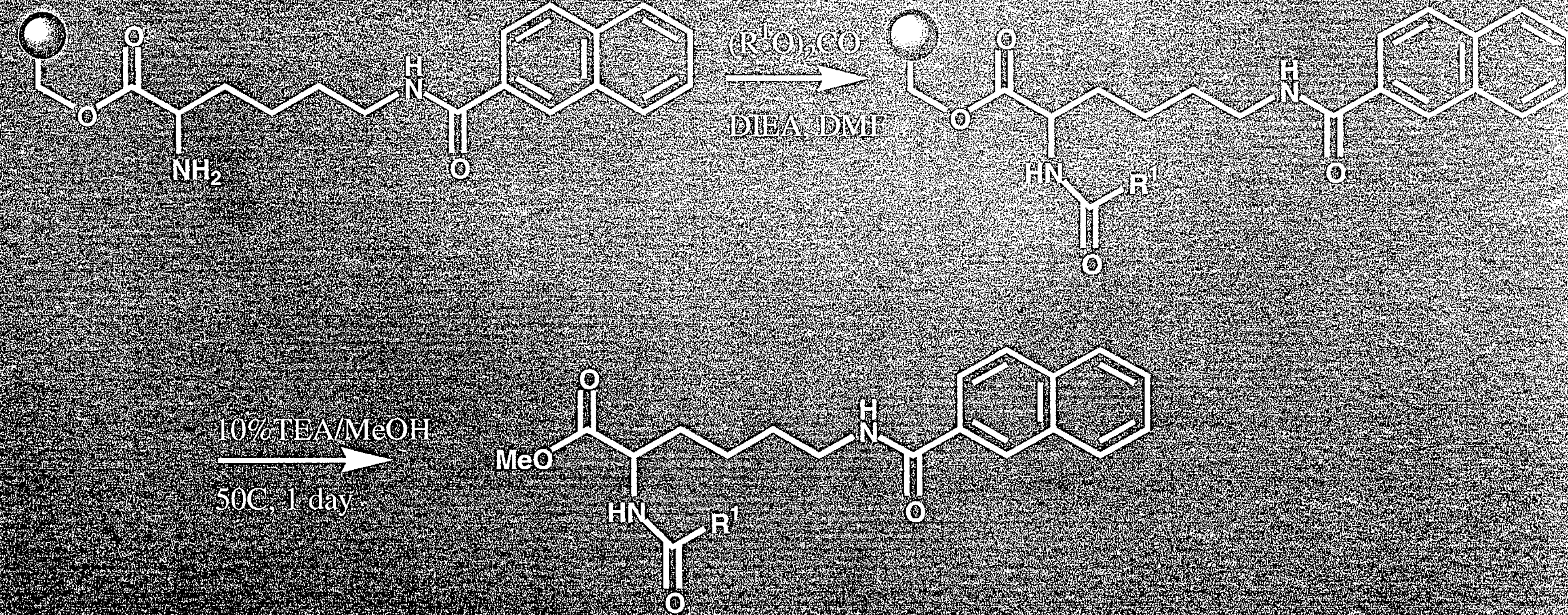
Cross Contamination Libraries



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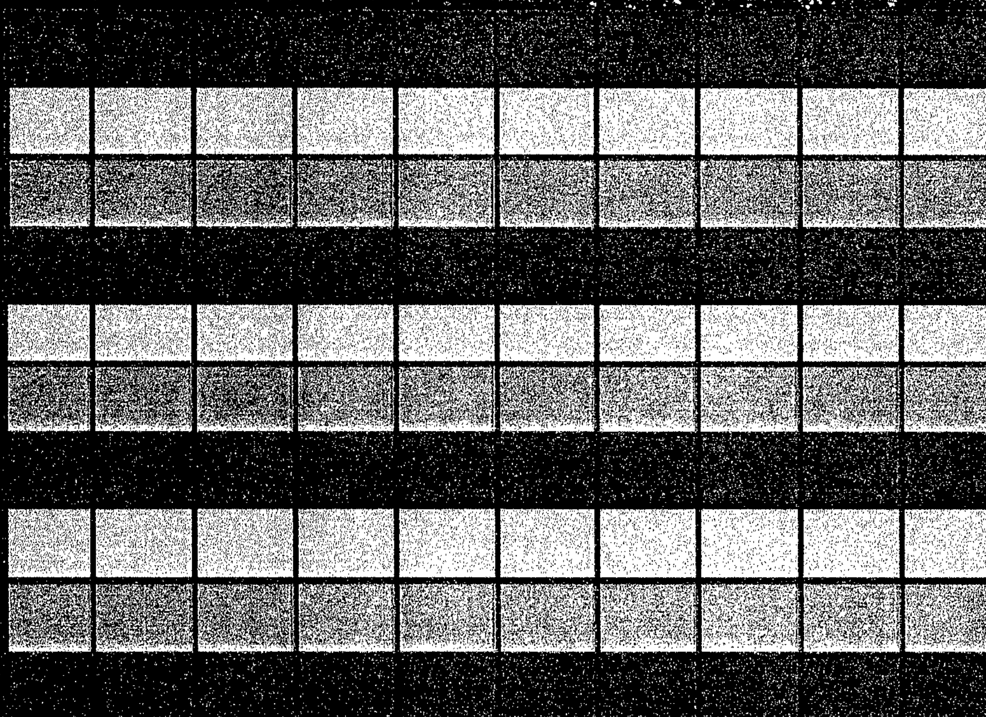
Layout of Cross Contamination



Row	Anhydride
2	None
3	Benzoic
4	2-Napthoic
5	None
6	Benzoic
7	2-Napthoic
8	None
9	Benzoic
10	2-Napthoic
	None

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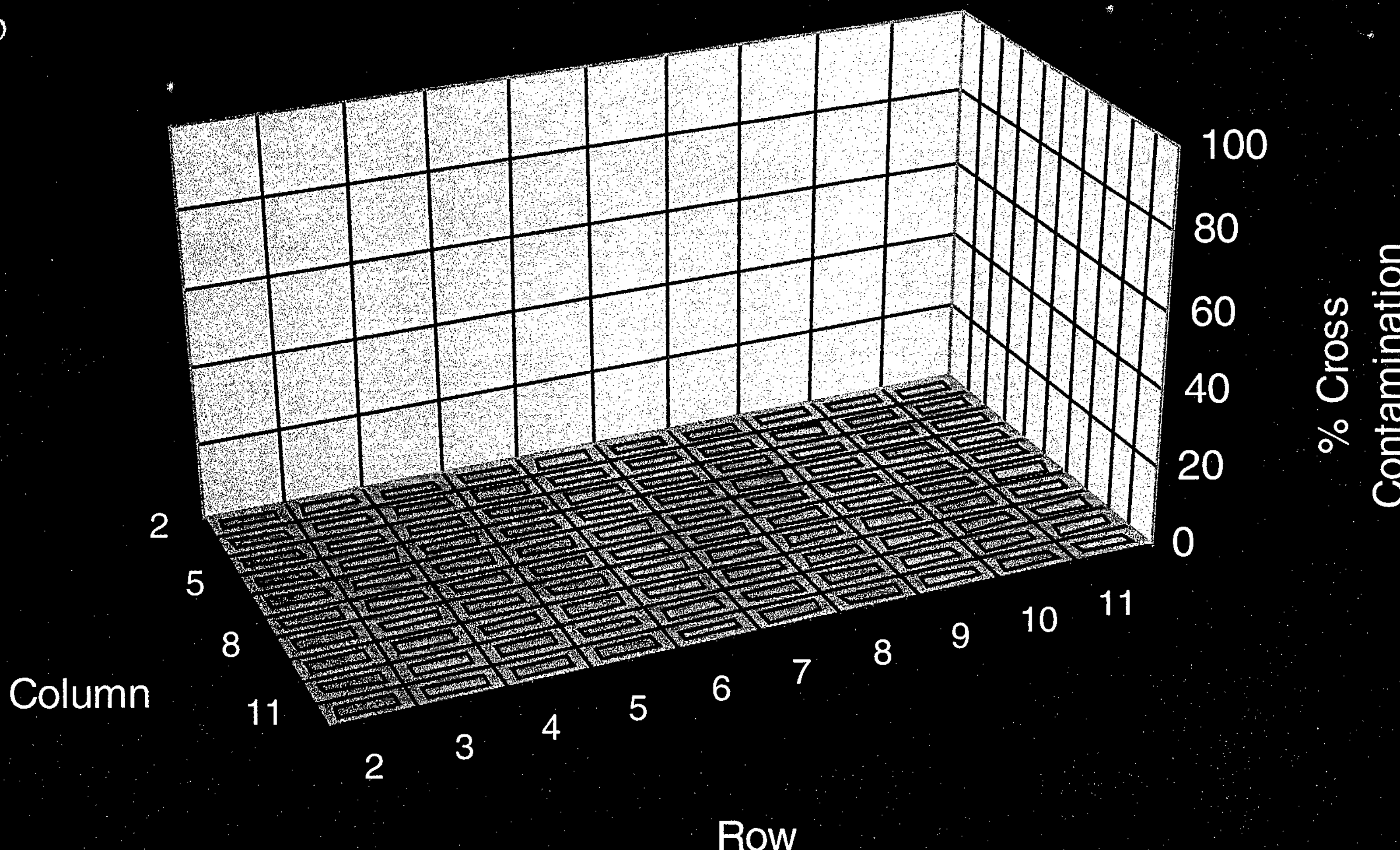
Cross-contamination after TFA System Purge



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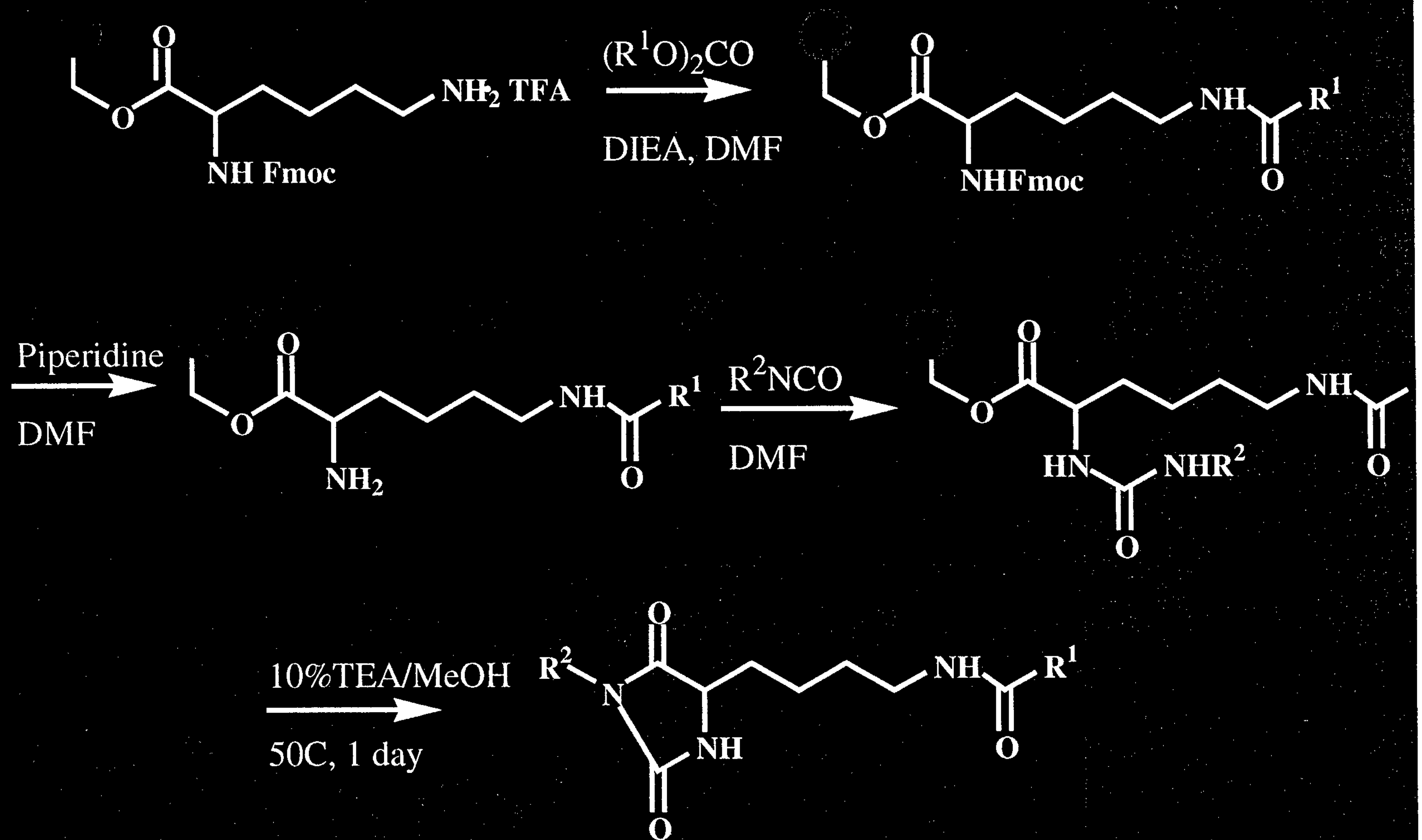
Hydantoin Reaction Scheme



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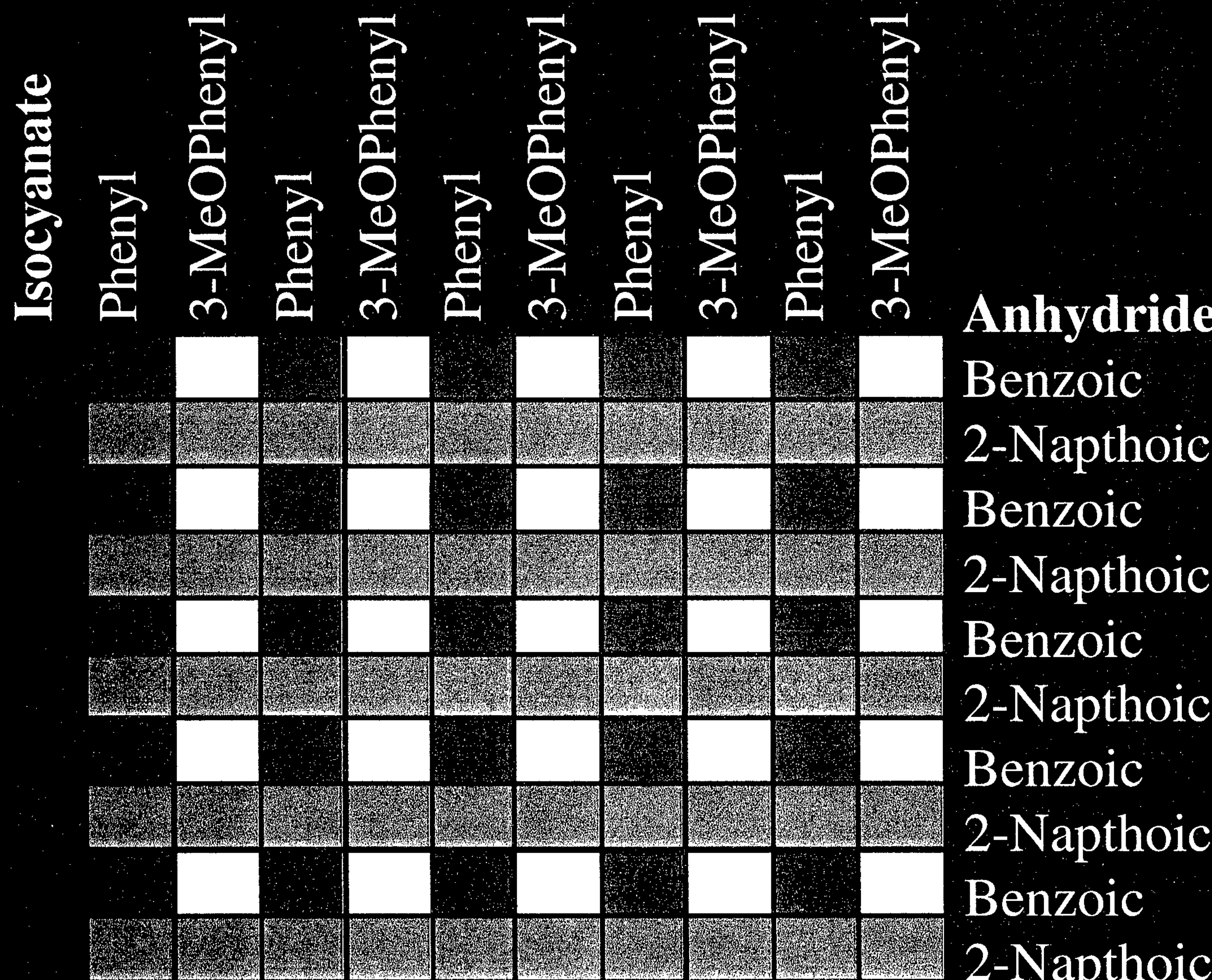
Layout of Fidelity Library



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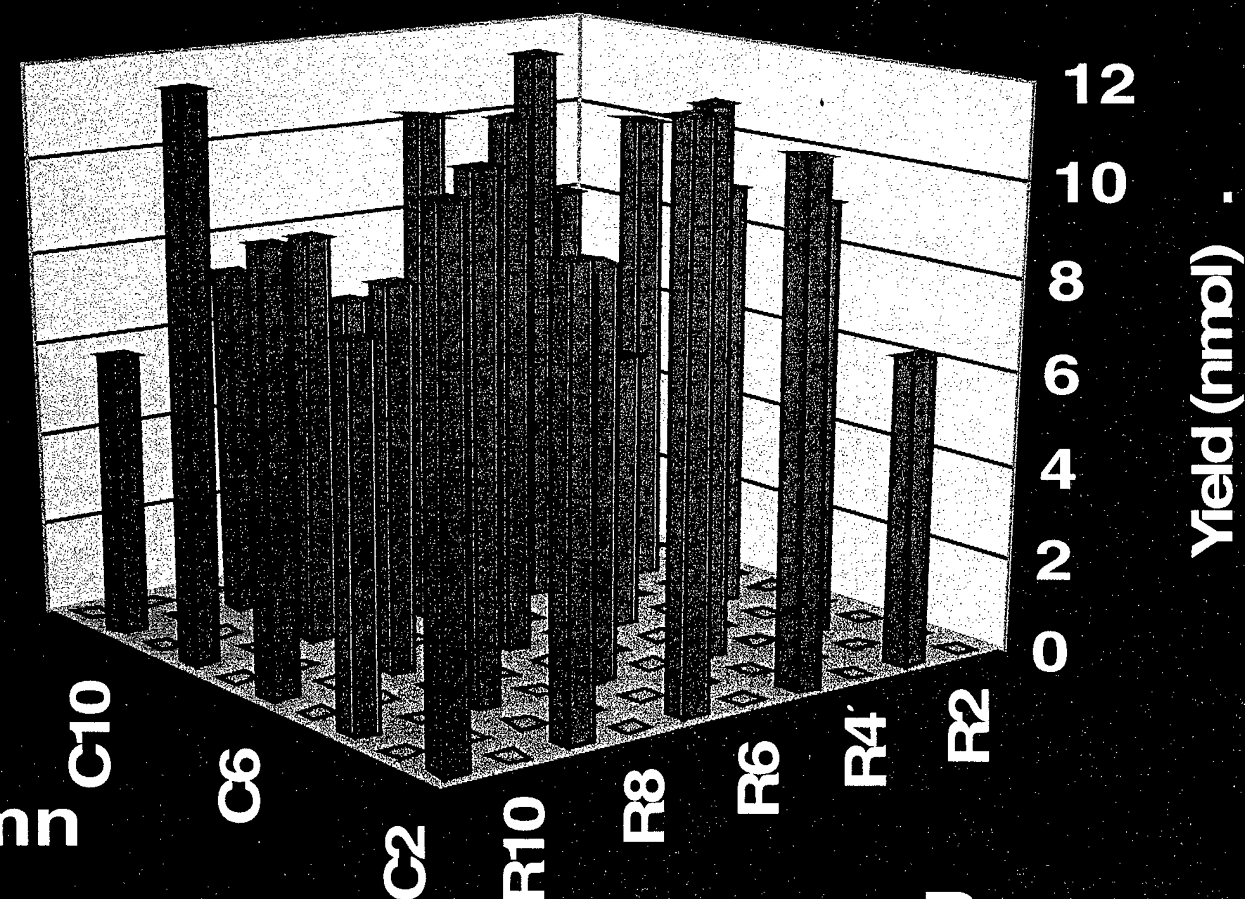
Fidelity Library Yields & Reproducibility



Layout of Hydantoin Library

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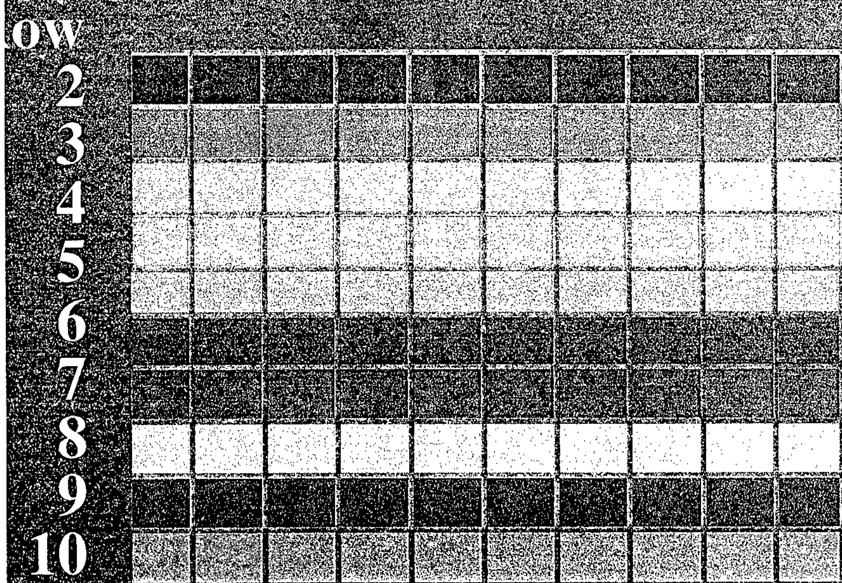
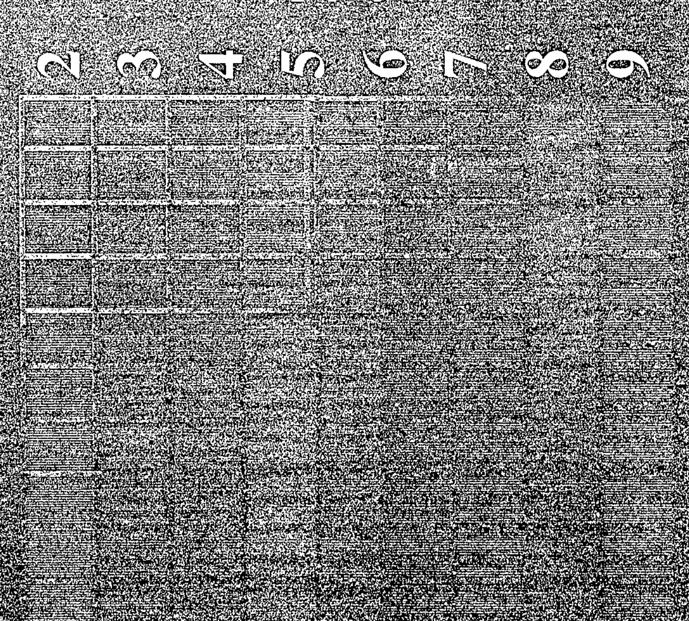
Step 1: 10 Anhydrides



Step 2: 10 Isocyanates



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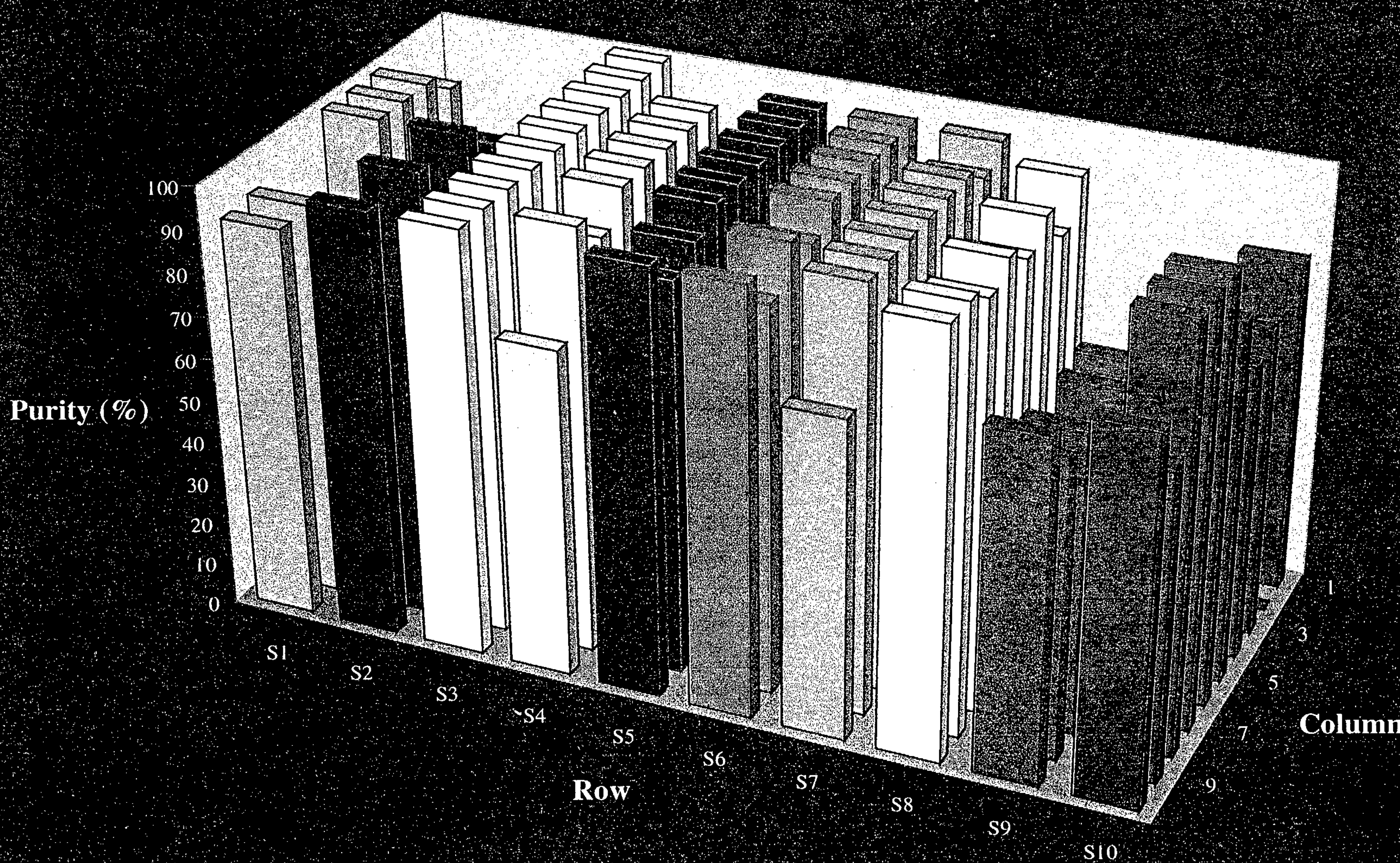
100 Compound Hydantoin Library



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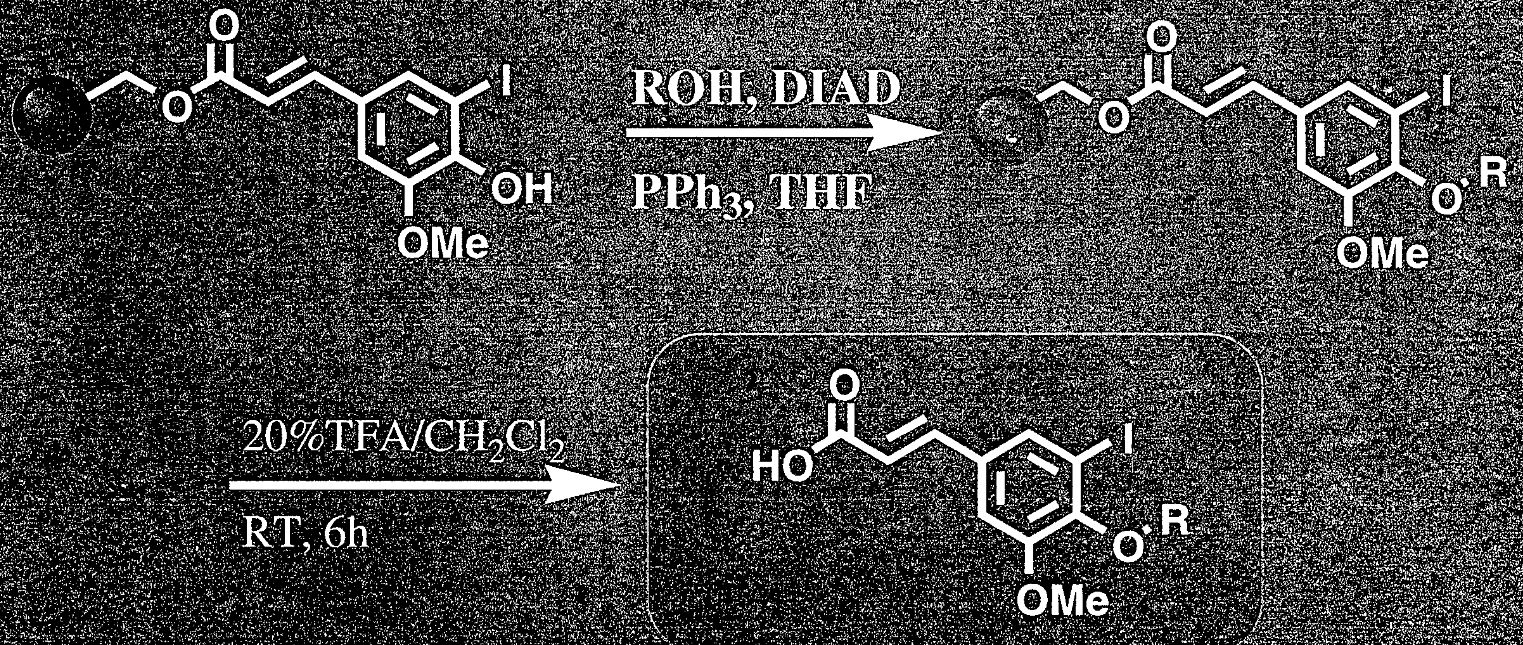
SPOS Reaction Optimization: Mitsunobu



Variables: Alcohol, Time, Concentration, Equivalents

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Reaction Kinetics of SPOS Mitsunobu

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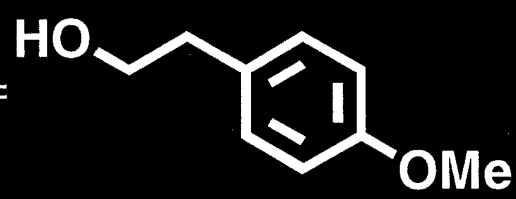
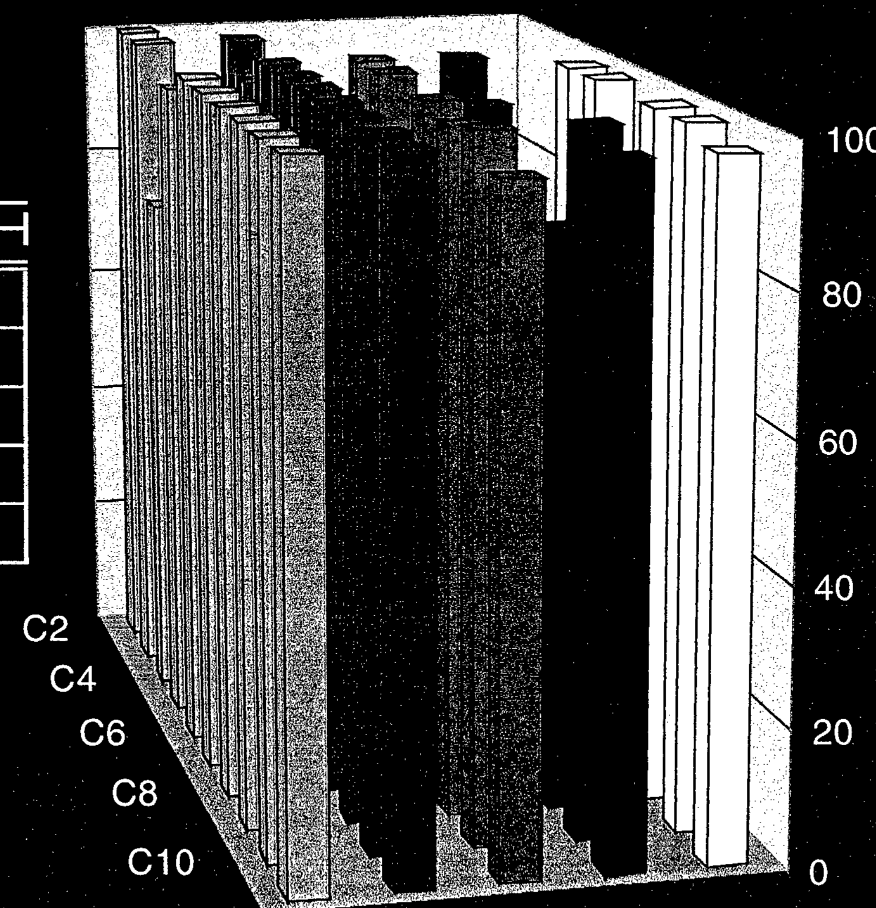
ROH = 

	Time (hr)	[ROH] (M)	Equiv ROH
	4	0.5	120
	1	0.5	120
	1	0.5	60
	1	0.1	24
	1	0.1	12



2 Beads = 20 nmol / 650 nl well

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Demonstrated Reaction Conditions

- Solid Phase Chemistry
- Solution Phase Chemistry
- Temperature Control (RT to 100°C)
- Hazardous Reaction Conditions (TFA)
- Sensitive Reaction Conditions (RNCOs)
- Purification by Resin Capture

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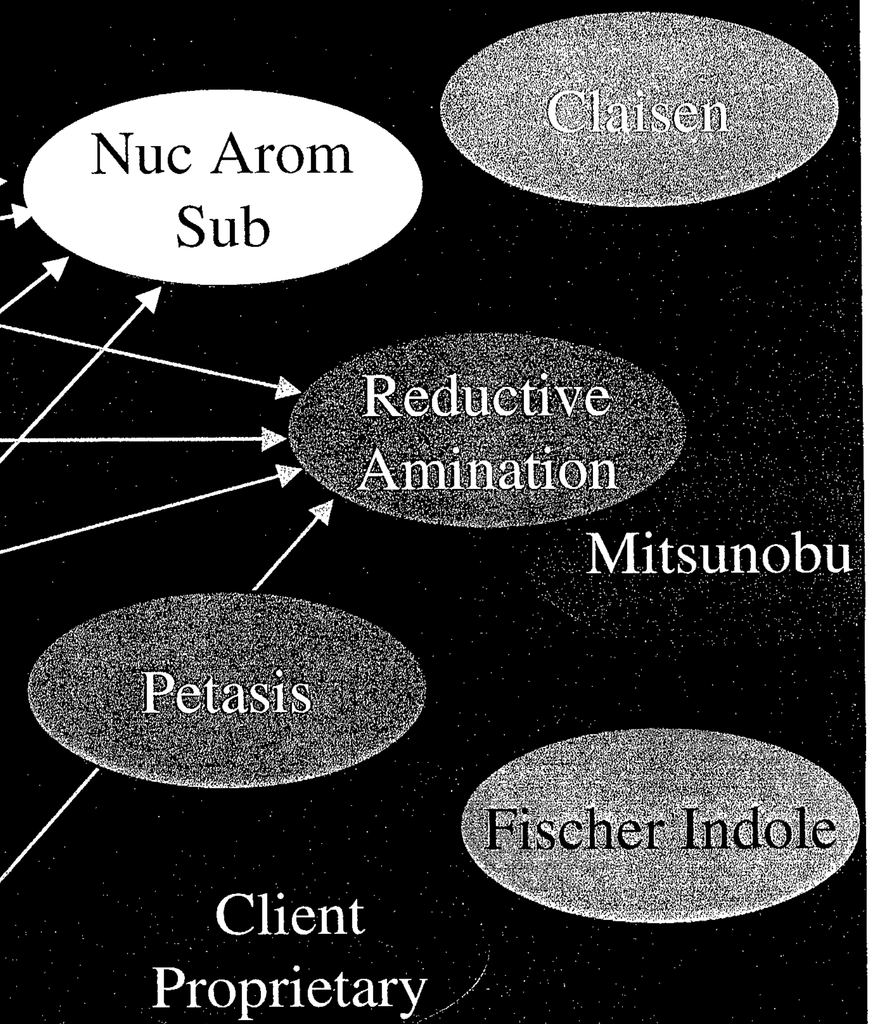
Representative Micro-Enabled Chemistry

<u>Customization Options</u>

- 100 Compounds
- Solid Phase
- Solution Phase
- Reaction Optimization
- Library Generation
- Elevated Temperature
- Multi-component Chemistry
- Purification by Resin Capture



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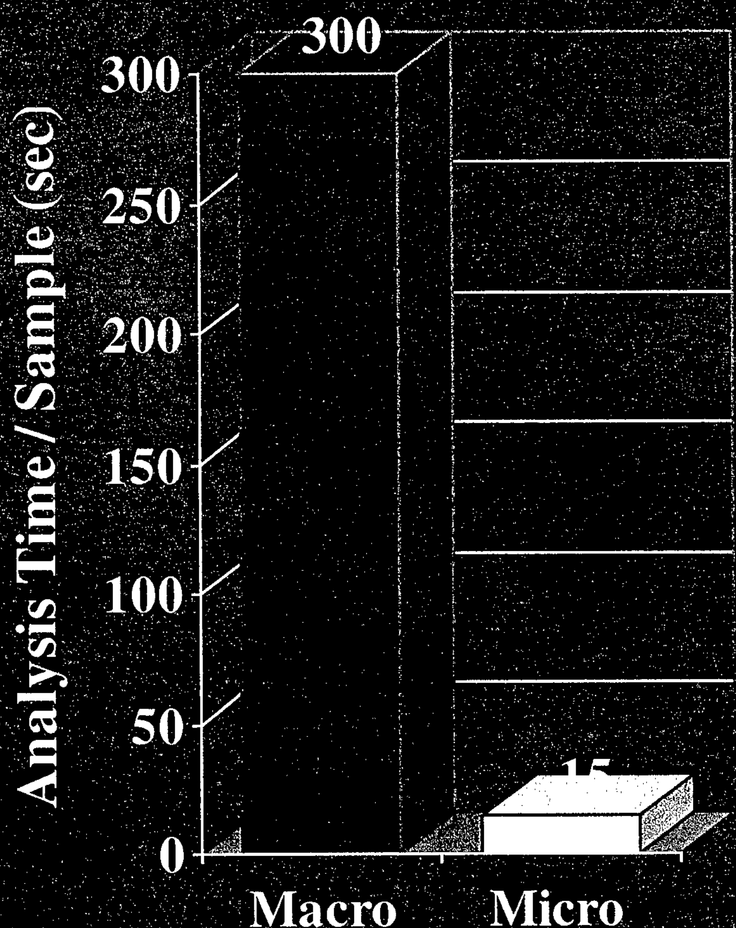
Analytical Needs: LC/MS Analysis for Synthesis or Metabolism



TOTAL SAMPLE AMOUNT
Macro =5 nmol
Micro < 0.01 nmol

TOTAL ANALYSIS TIME
10,000 Samples / Drug
Macro =100 days
Micro = 5 Days

95% Reduction in Time
$95 Million Savings in Development

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Analytical Collaboration: Advanced Bioanalytical Services (ABS)

Accelerate Drug Discovery Efforts
- Increase Sample Throughput >20x
- Decrease Sample Quantity Requirement >500x
- Enable Micro to Micro Interface
- Provide Purity and Characterization Information

Access to Proprietary Technology and Know-How
- CRO Organization for ADME assay analyses (LC/MS)
- President (Jack Henion) is Inventor of LC/MS
- Intellectual Property for nanospray MS off chip

Market Opportunities
- Integrated Synthesis & Analysis
- Transport Chips (disposable)
- Future ADME Applications

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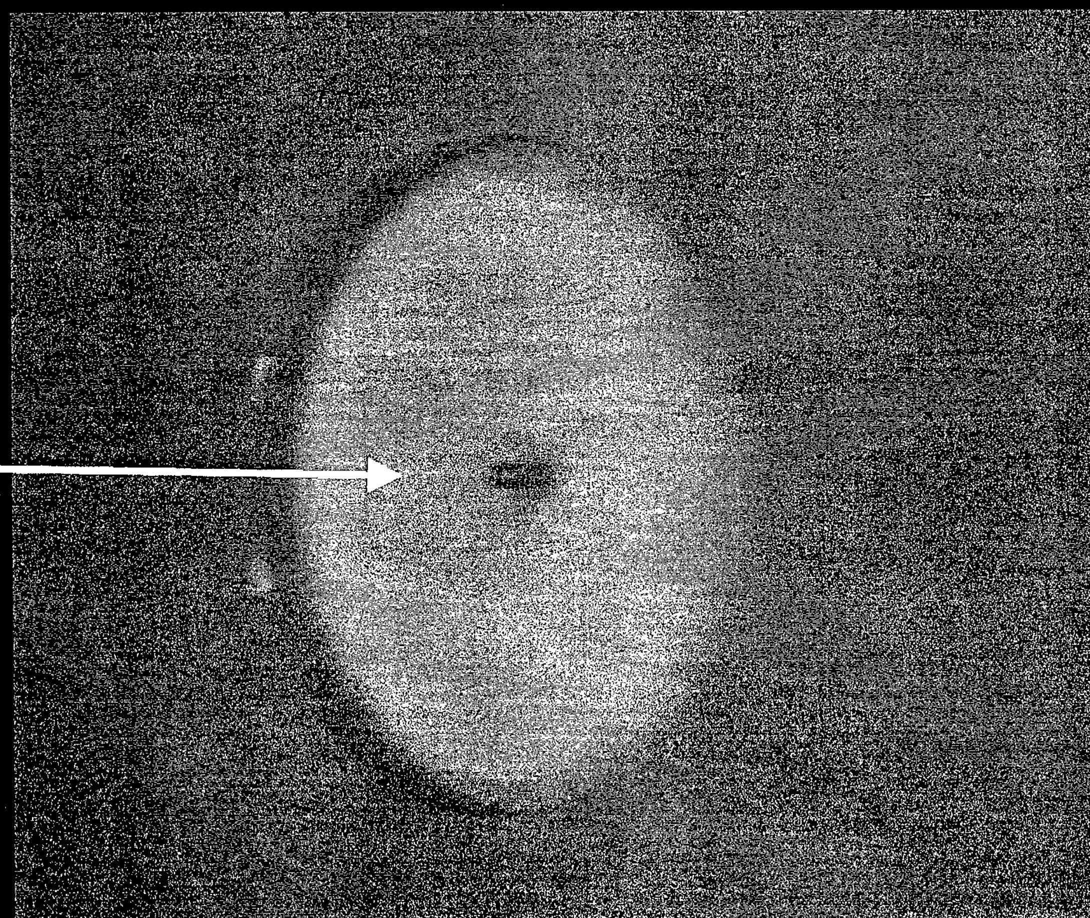
ABS Microchip-Based Electrospray MS Nozzle in Silicon



Nozzle
ID = 20 um
OD = 28 um
Ht = 50 um

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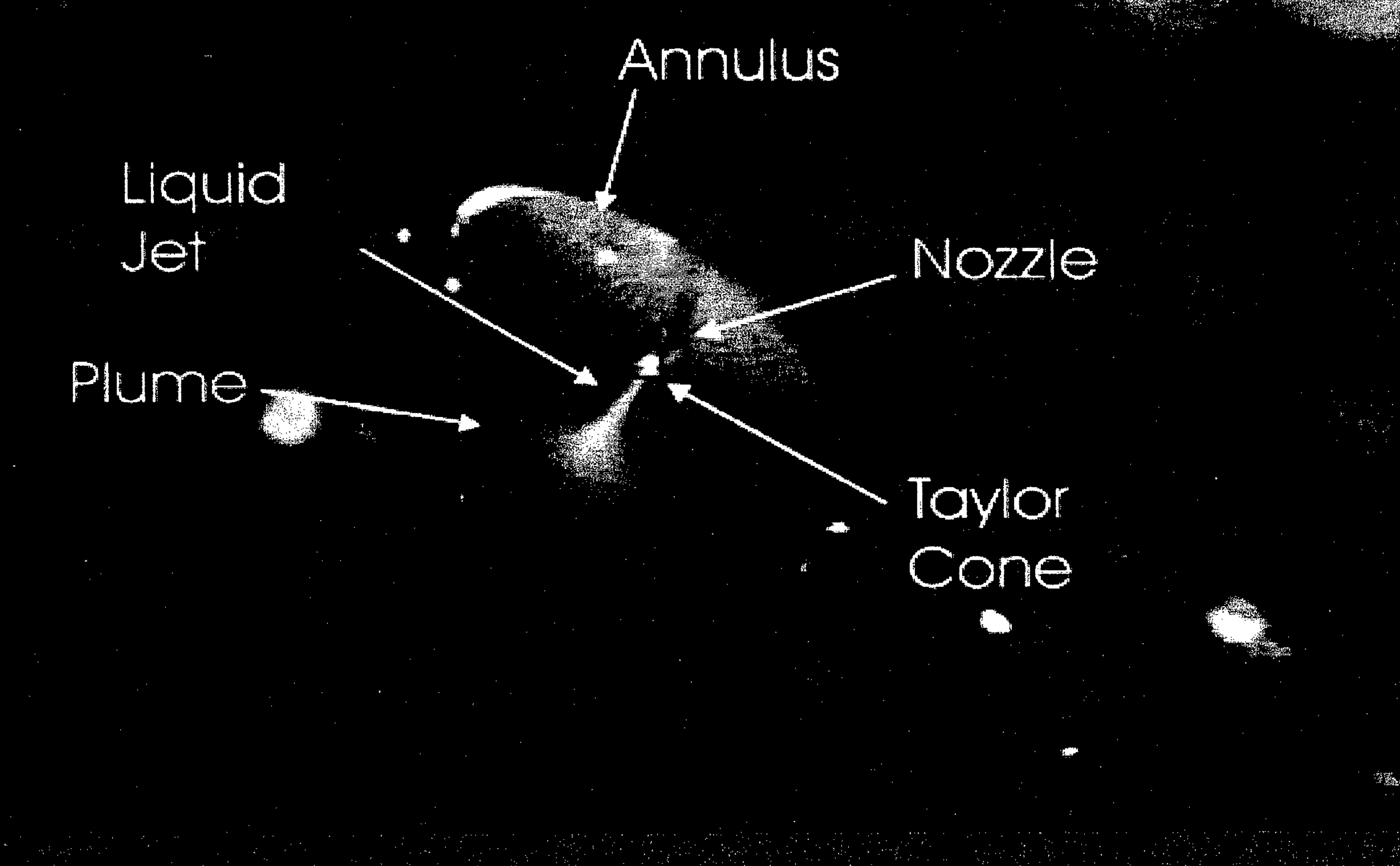
ABS Electrospray off Chip

Nanospray at 100 nL/min



Integrated Synthesis & Analysis

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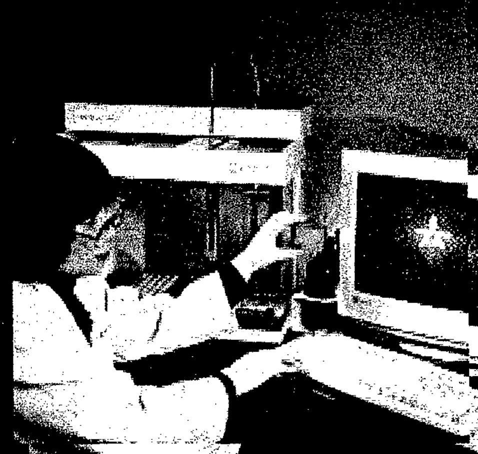
Chemtel Chip



ChemStream™

ESI/MS Chip

MassStream ™

Reaction Optimizatio
Lead Optimization
Lead Generation
Quantitative HTS

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Accomplishments

ABS

- Chemistry
  - SPOS Reaction Optimization -4 variables / 10 reps
  - SPOS Libraries - 100 compounds / 4 steps
  - Solution Phase Libraries - 100 compounds / 1 step
  - Purification by Resin Capture - 100 compounds
- Analysis
  - Low voltage electrospray
  - Low dead volume
  - ESI / MS from Chip - Reserpine / 1 nozzle
  - ESI / MS from Chip - Orchid Compounds / 1 nozzle

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Future of Microfluidics & Chip Technology

- Increasing Parallel Processing
- Ever Higher Densities
- More Sensitive Cost Analyses
- Significant Informatics Needs
- Lower Barriers to Entry
- Compatibility with Industry Standards (i.e. 96)
- Integration

Gas Phase Chemical Detection with μChemLab™ :

An Integrated Chemical Analysis System

Steve Casalnuovo
Microsensors Research and Development Dept.
Sandia National Laboratories
Albuquerque, NM

505-844-6097
sacasal@sandia.gov

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Co-Workers

Greg Frye-Mason	Rich Kottenstette
Ed Heller	Carolyn Matzke
Pat Lewis	Ron Manginell
Albert Baca	Susan Hietala
Vince Hietala	Darryl Sasaki
John Reno	Kent Schubert

Sandia National Laboratories

µChemLab™

What it is (and isn't)

Where it is

Where it's going

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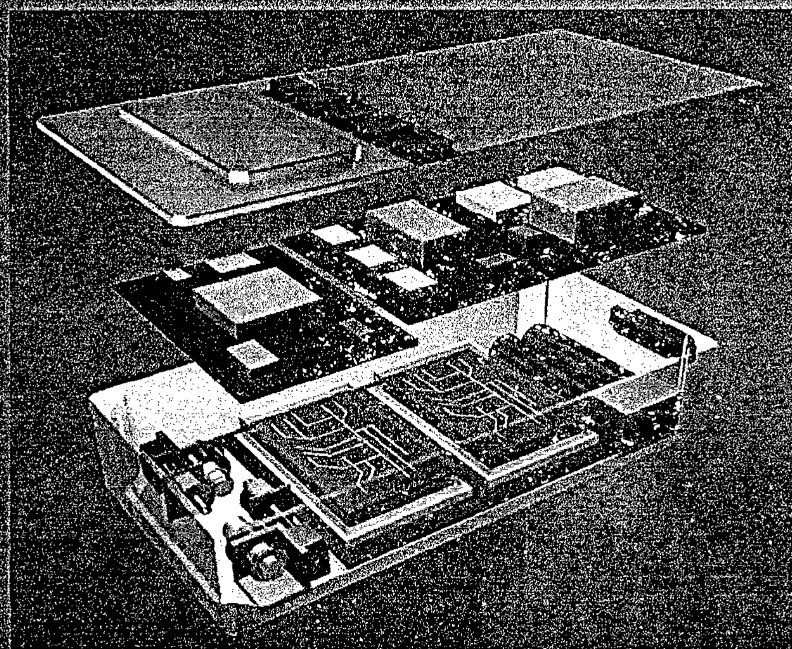
What it is: a hand-held, battery-powered, liquid and gas phase chemical detection system.



← 9 in →

What it isn't: 1) a chem lab on a chip (several chips and a lot of system hardware).
2) a micro-reactor (but almost).

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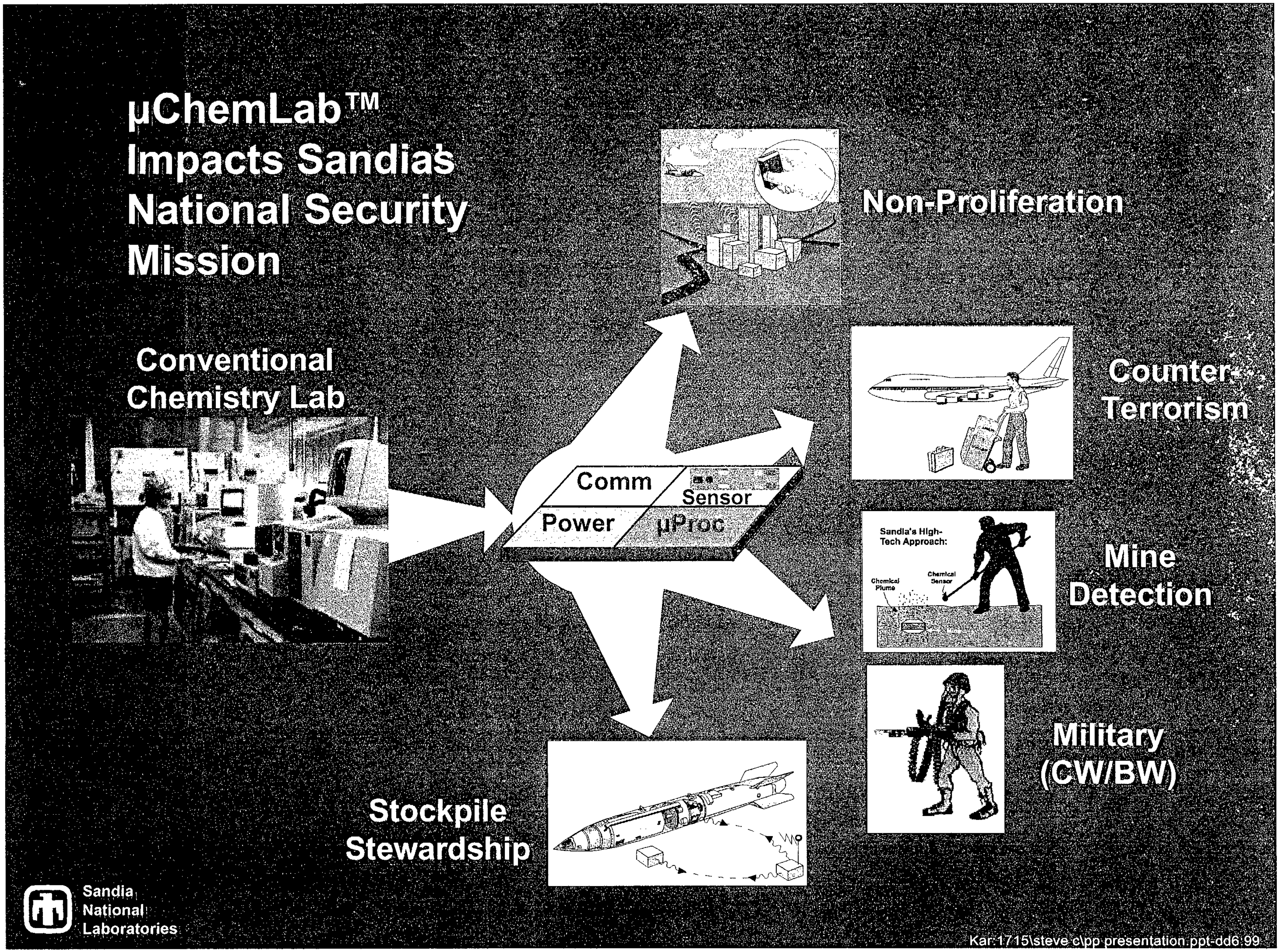
μChemLab™ Impacts Sandia's National Security Mission
Conventional Chemistry Lab
Comm
Sensor
Power
μProc
Non-Proliferation
Counter-Terrorism
Sandia's High-Tech Approach:
Chemical Plume
Chemical Sensor
Mine Detection
Military (CW/BW)
Stockpile Stewardship
Sandia National Laboratories
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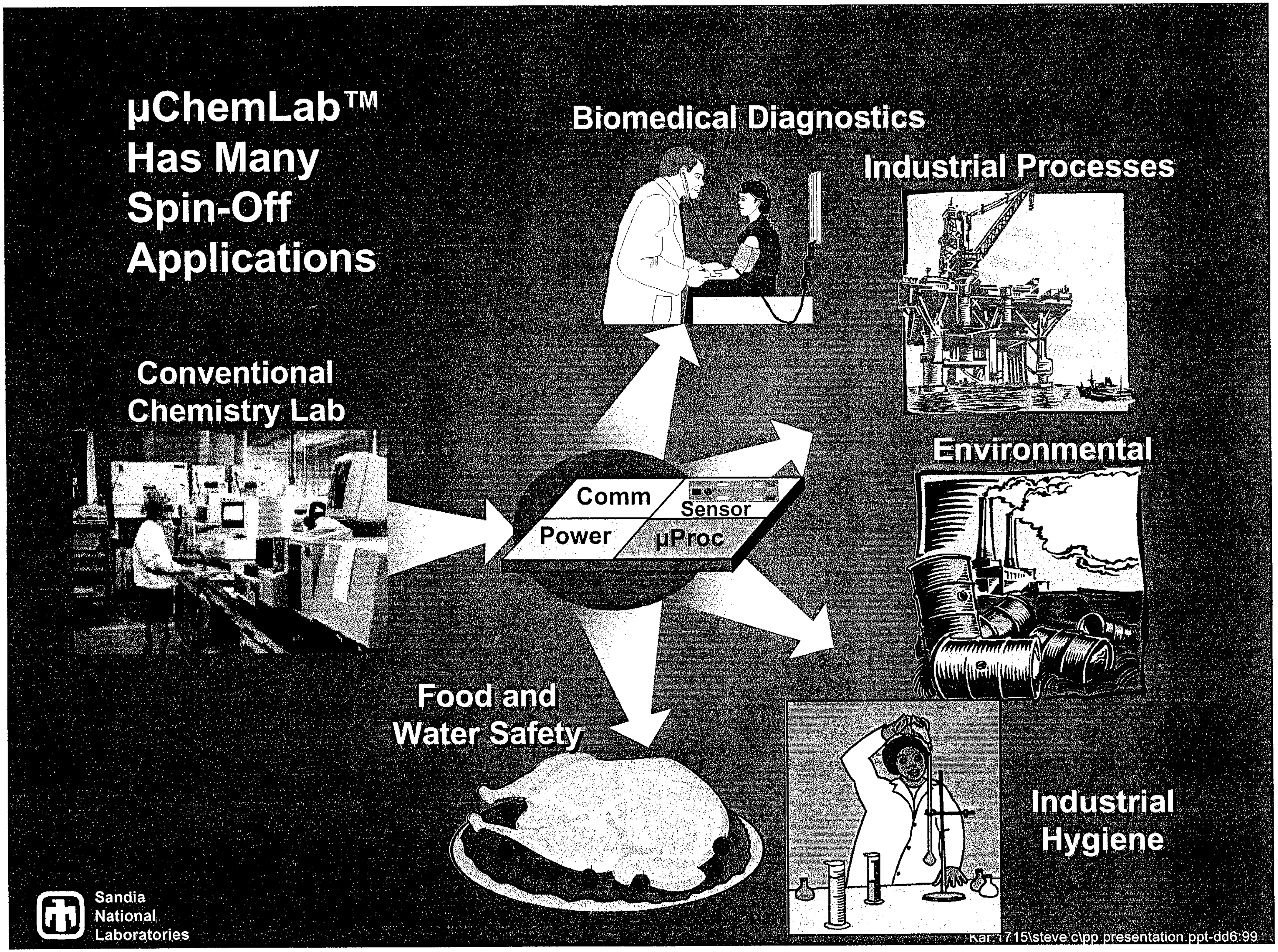
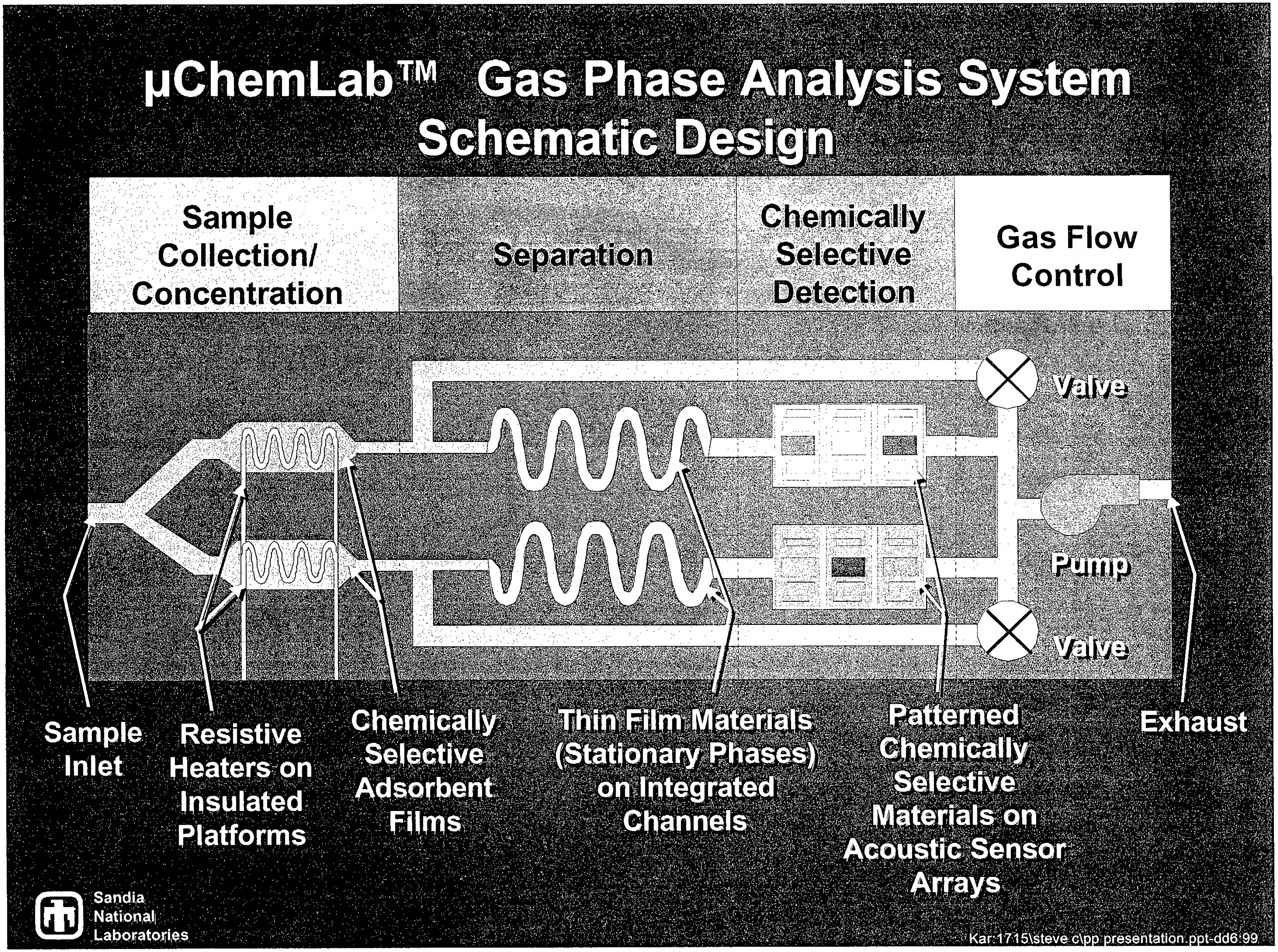
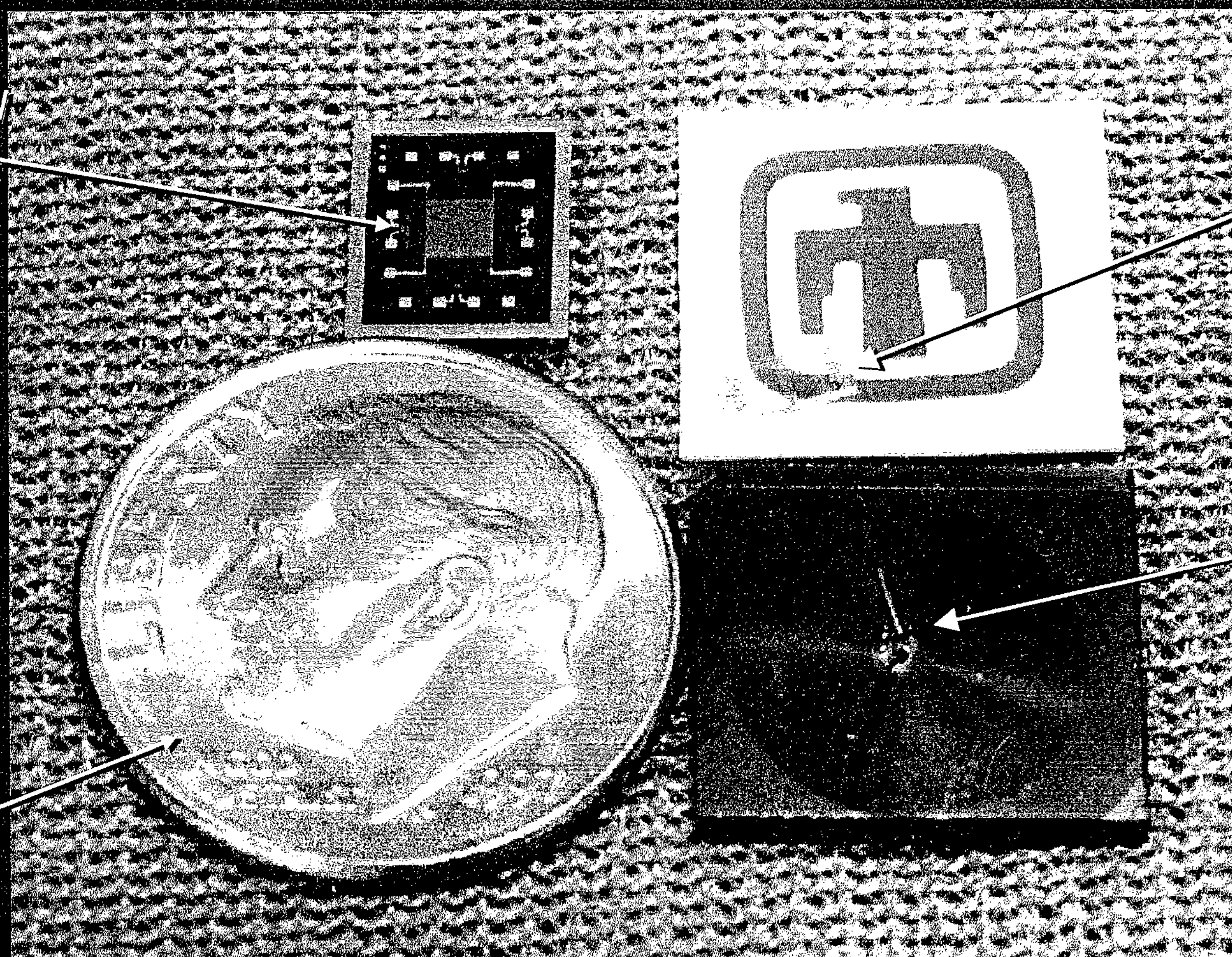

µChemLab™
Has Many
Spin-Off
Applications
Biomedical Diagnostics
Industrial Processes
Conventional
Chemistry Lab
Environmental
Comm
Sensor
Power
µProc
Food and
Water Safety
Industrial
Hygiene
Sandia
National
Laboratories
Kar: 1715\steve c\pp presentation.ppt-dd6:99


μChemLab™ Gas Phase Analysis System
Schematic Design
Sample Collection/ Concentration
Separation
Chemically Selective Detection
Gas Flow Control
Valve
Pump
Valve
Sample Inlet
Resistive Heaters on Insulated Platforms
Chemically Selective Adsorbent Films
Thin Film Materials (Stationary Phases) on Integrated Channels
Patterned Chemically Selective Materials on Acoustic Sensor Arrays
Exhaust
Sandia National Laboratories
Kar:17:15\steve c\pp presentation.ppt-dd6 99

Miniature Chemical Analysis Components are Fabricated in Sandia's Compound Semiconductor Research Lab



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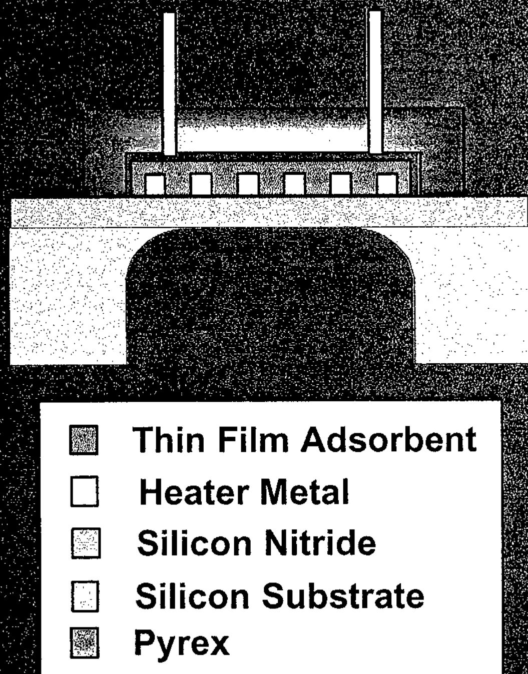
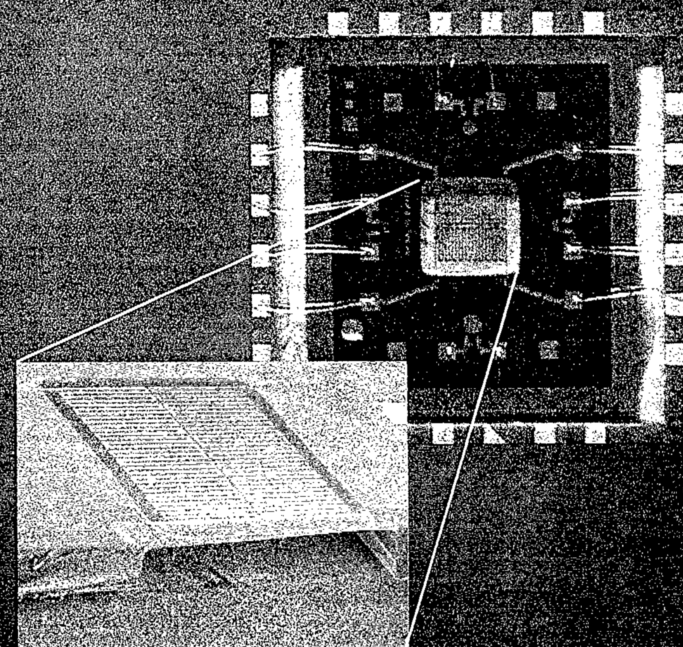
Concentrator

Purpose: To selectively concentrate all analytes relative to interferants.

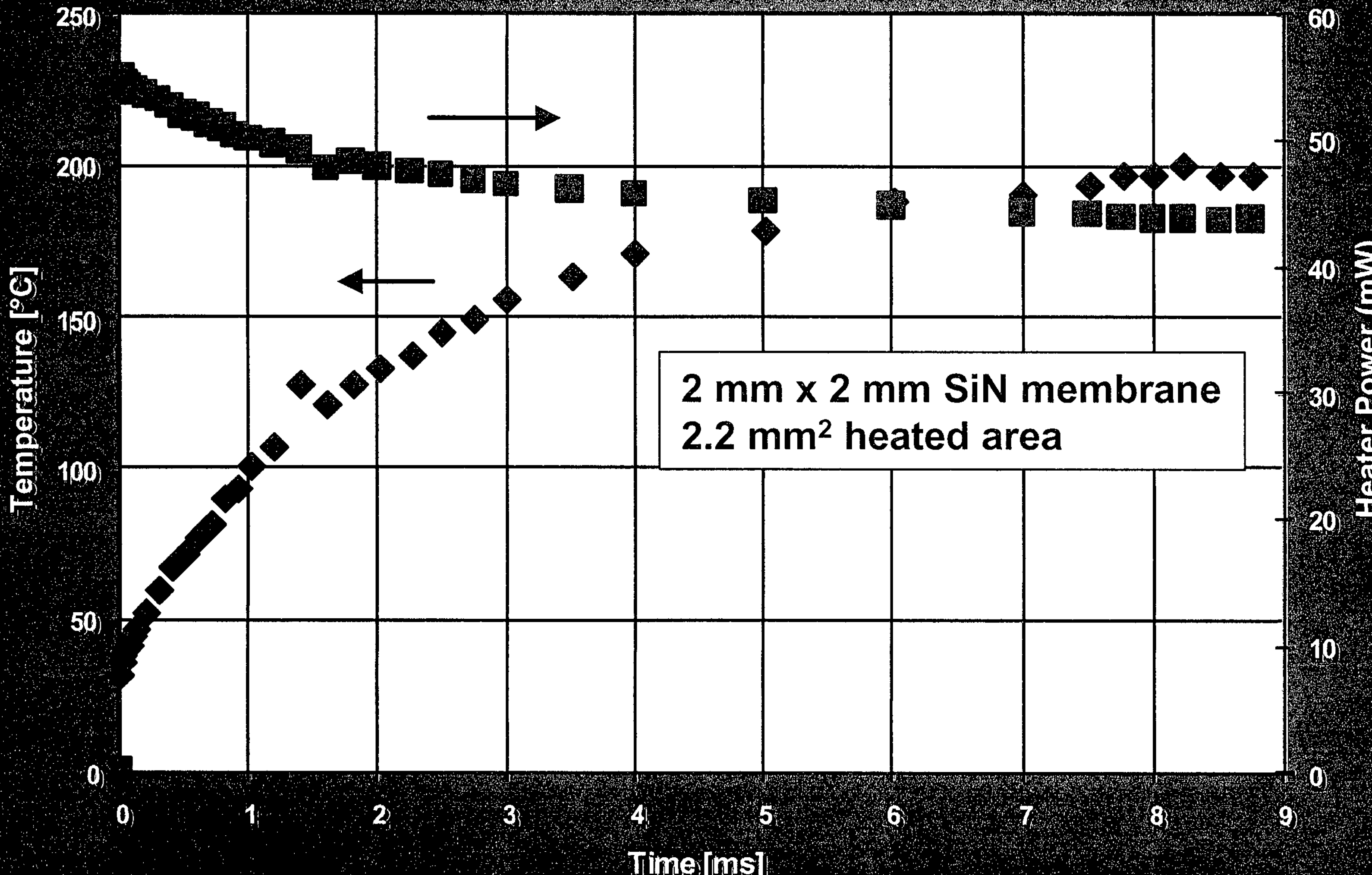
Design: Micromachined hotplate with thin film adsorber on Si_3N_4 membrane for low heat capacity and high thermal isolation.

Fabrication: Si bulk micromachining with DRIE.





Rapid Heating at Low Power Using Microfabricated Concentrator



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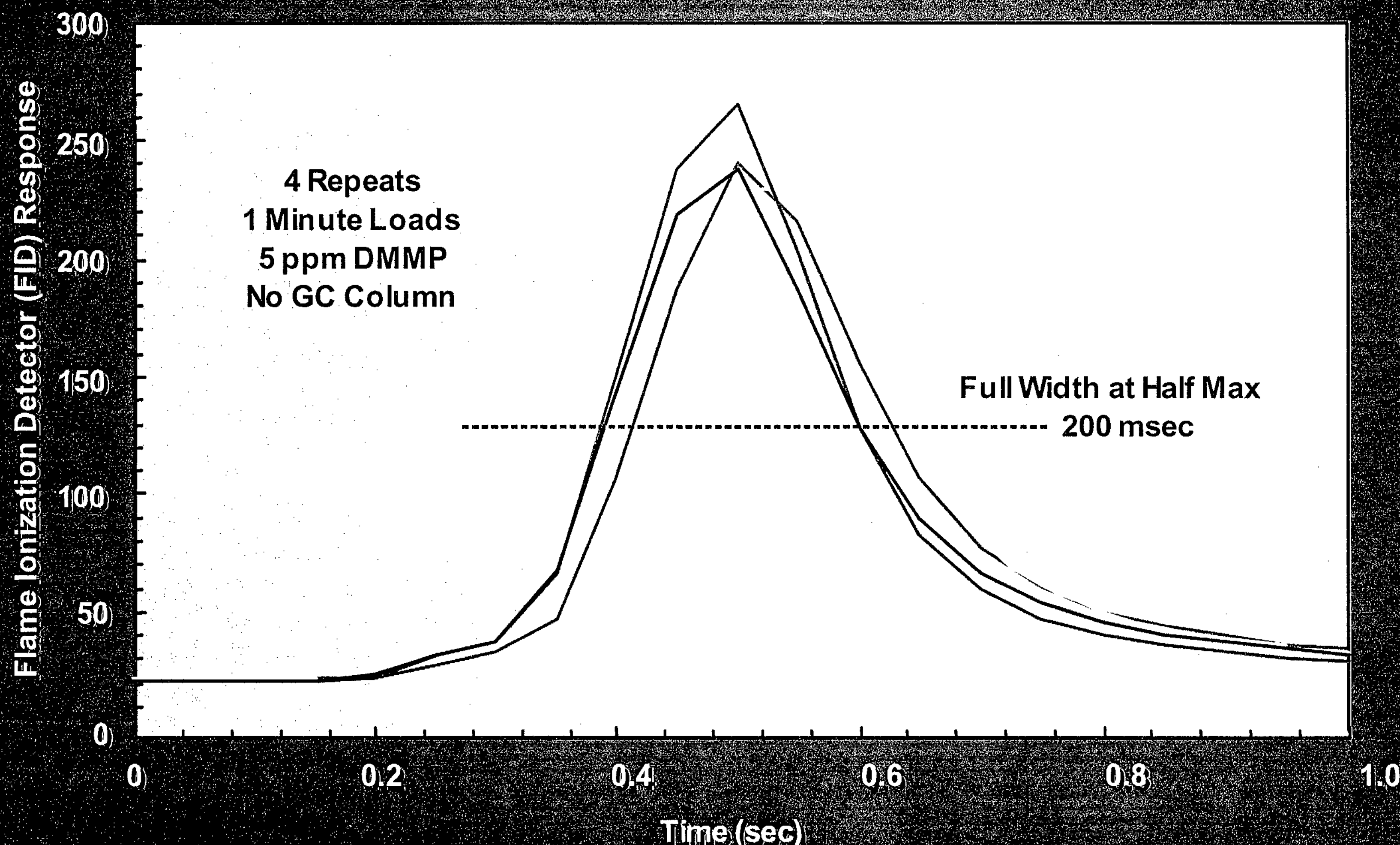
Rapid Thermal Desorption from Micromachined Concentrator



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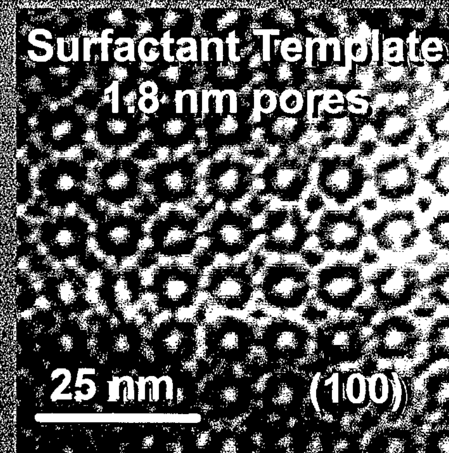
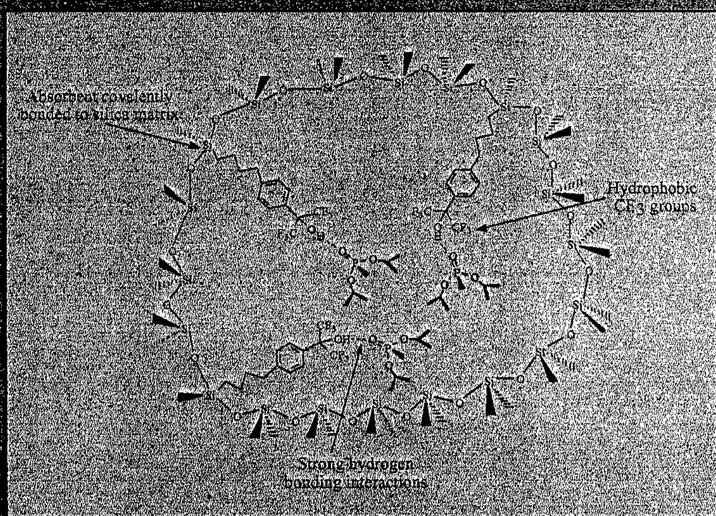
Tailored Sol-Gel Materials Provide Thin Film Adsorbents with High Uptake and Chemical Selectivity

Tailored Porosity

- Controlled Pore Size (1-5 nm range)
- High Surface Area (>1000 m^2/g)
- 100-1000 fold increase in uptake over polymer films





Tailored Surface Chemistry

- Polar oxide surfaces
- Nonpolar organic surfaces
- Hydrogen bond acidic surfaces
  - Hexafluoroalcohol derivative developed for nerve agents (similar to chemistry demonstrated using polymers by NRL and others)

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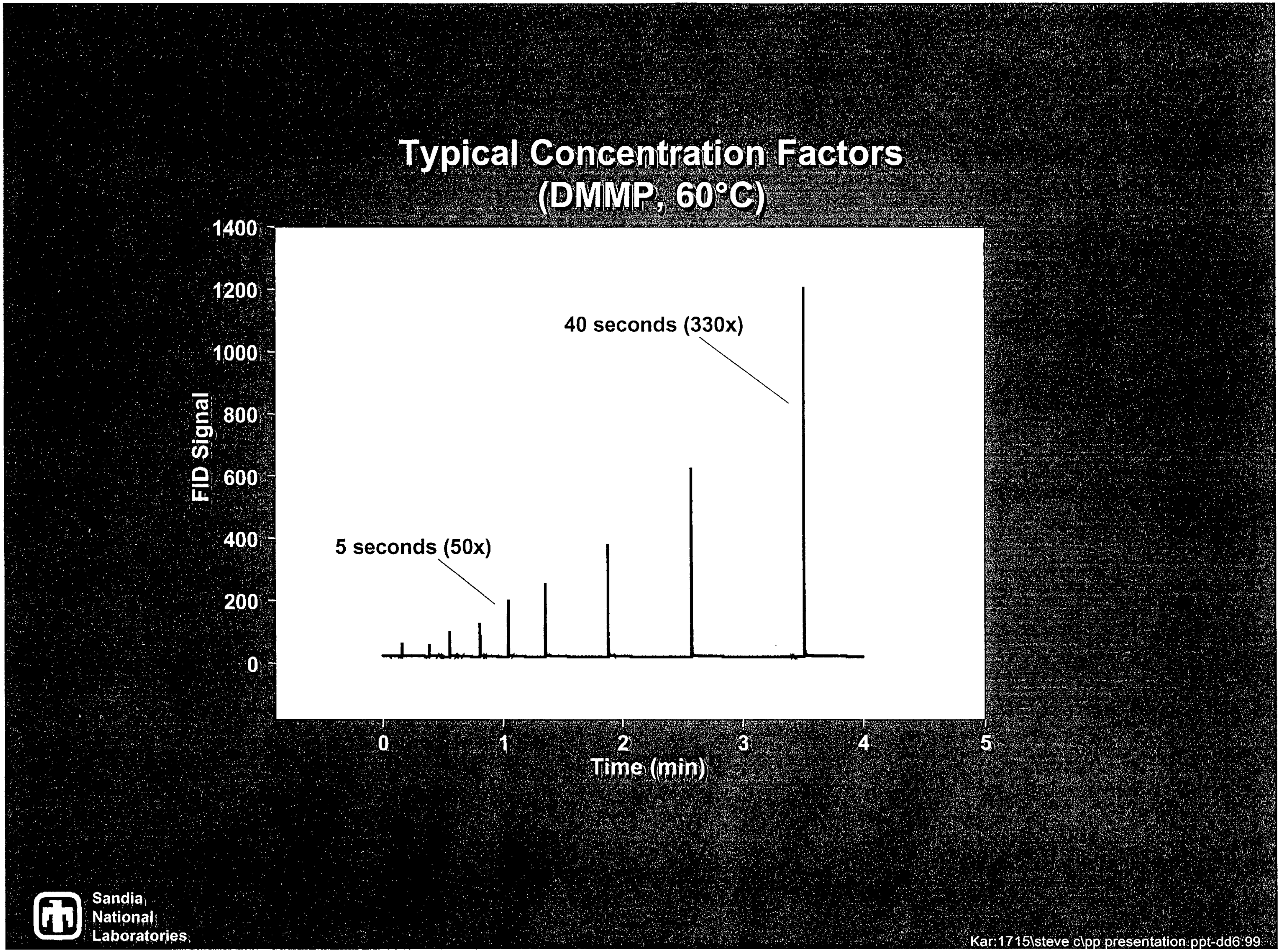
Typical Concentration Factors
(DMMP, 60°C)
FID Signal
1400
1200
1000
800
600
400
200
0
5 seconds (50x)
40 seconds (330x)
0
1
2
3
4
5
Time (min)
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Kar:1715\steve c\pp presentation.ppt-dd6:99

Concentration Factors for Various Simulants and Interferants

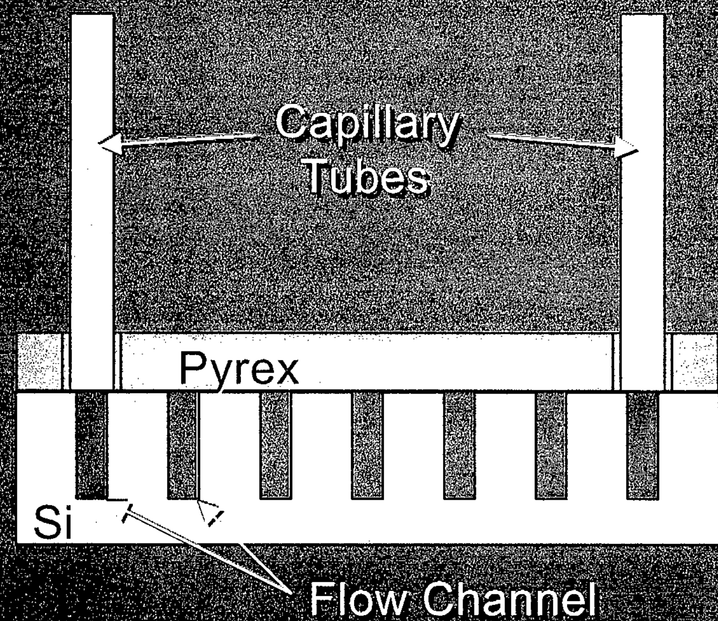
	Hydrophilic Thick	Hydrophilic Thin	Hydrophobic	Phenyl (micropore)
DMMP	310	510	540	400
CEPS	NM	58	100	140
Xylene	NM	8	13	31
MEK	NM	18	21	10

GC Column

Purpose: To provide temporal separation of analytes and interferants.

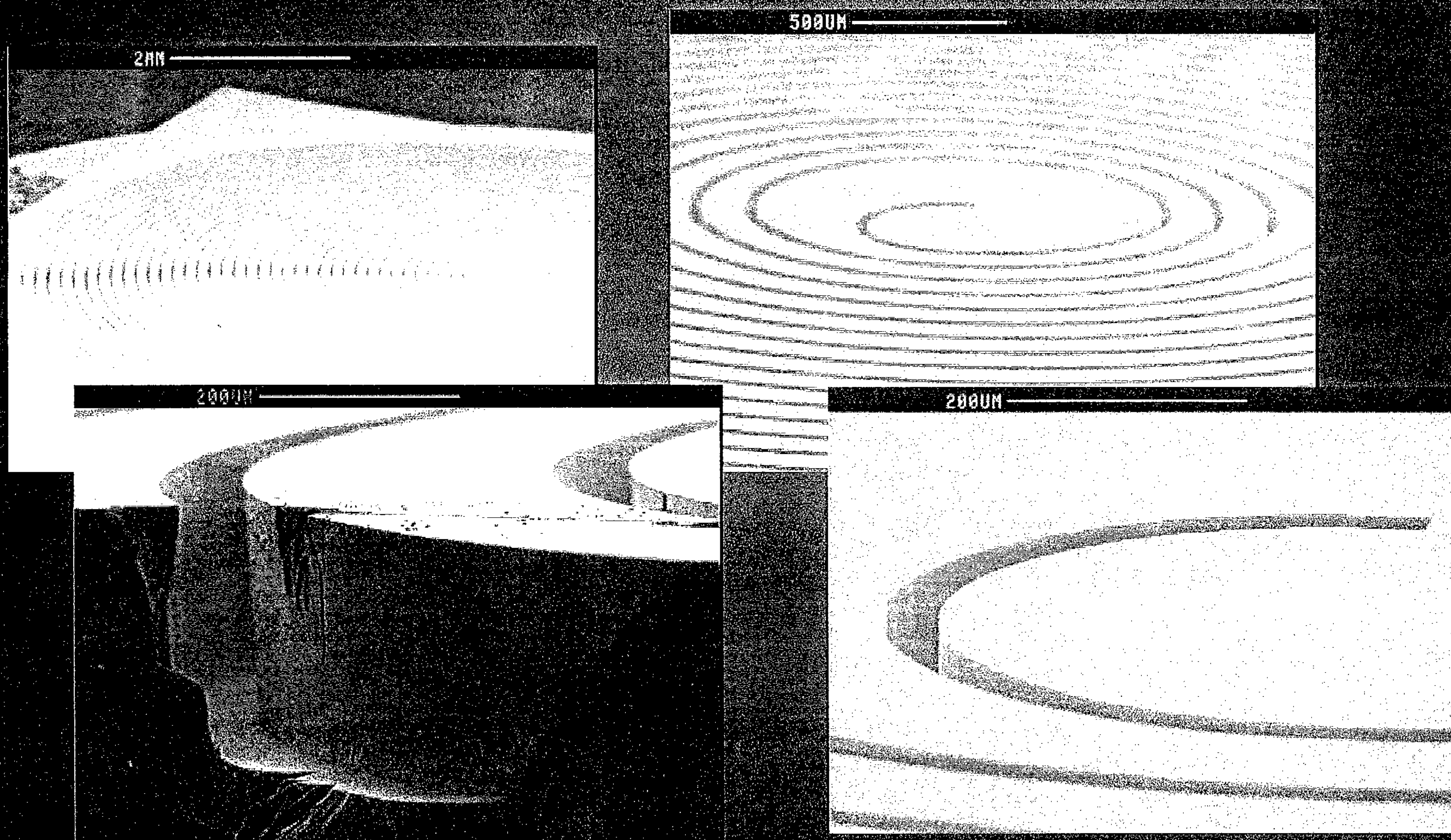
Design: Deep, narrow spiral channels in Si.

Fabrication: Anisotropic Si DRIE with anodically bonded Pyrex lid. Stationary phase coated onto thermally oxidized channel walls.



Cross-Section

Microfabricated GC Column:
1 m Long Column in 1 cm^2 using Si DRIE



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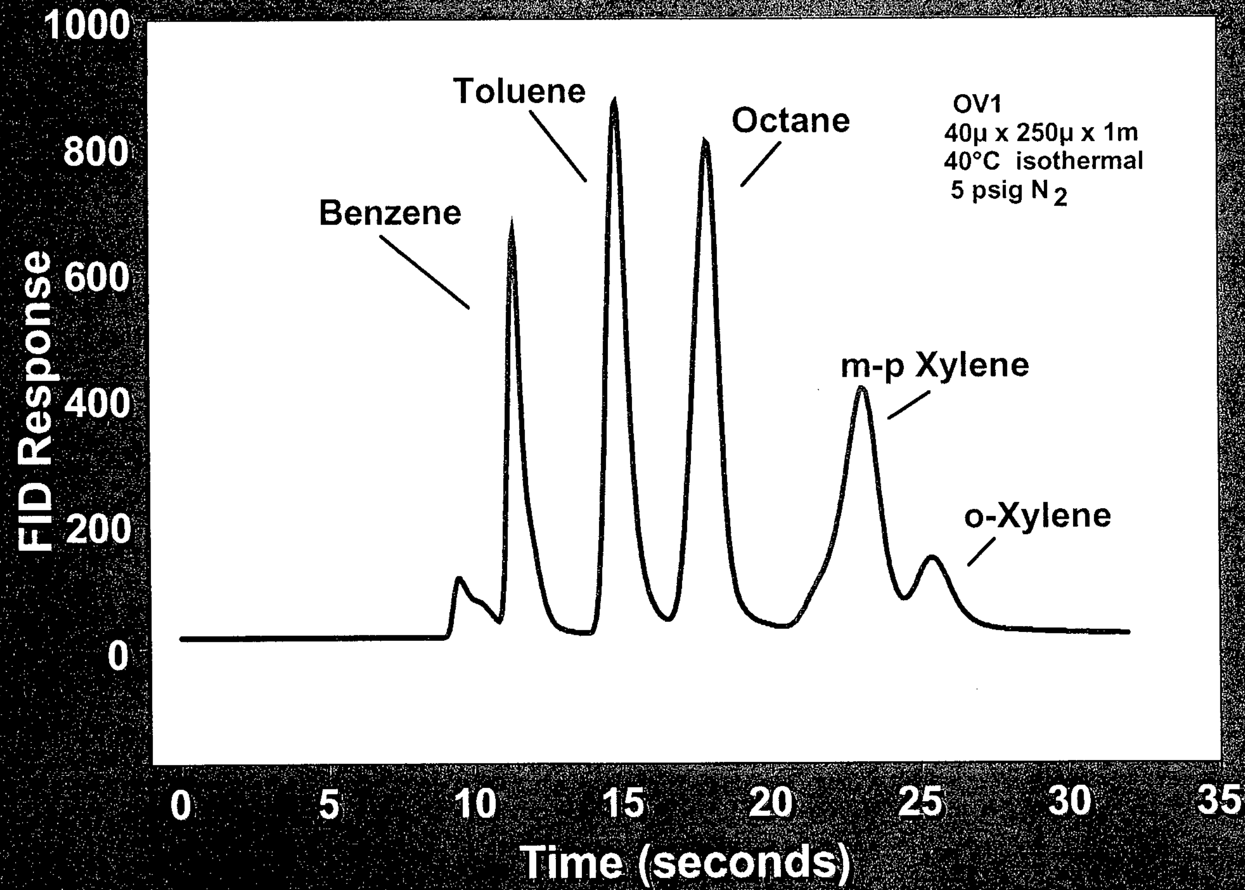
High Speed Separation of Common Hydrocarbons Using Microfabricated GC Column



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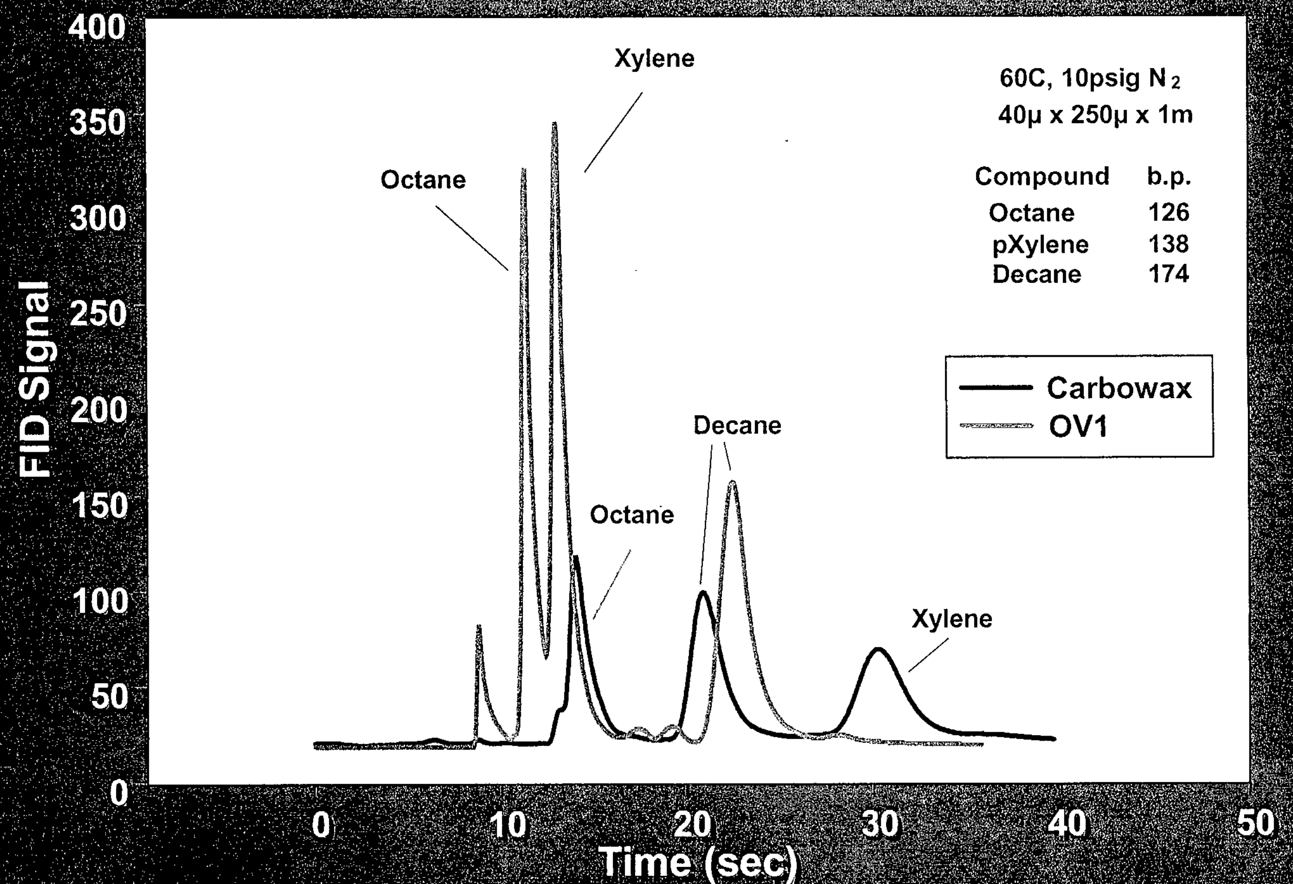
Dual GC Columns with Different Stationary Phases Provide Improved Discrimination



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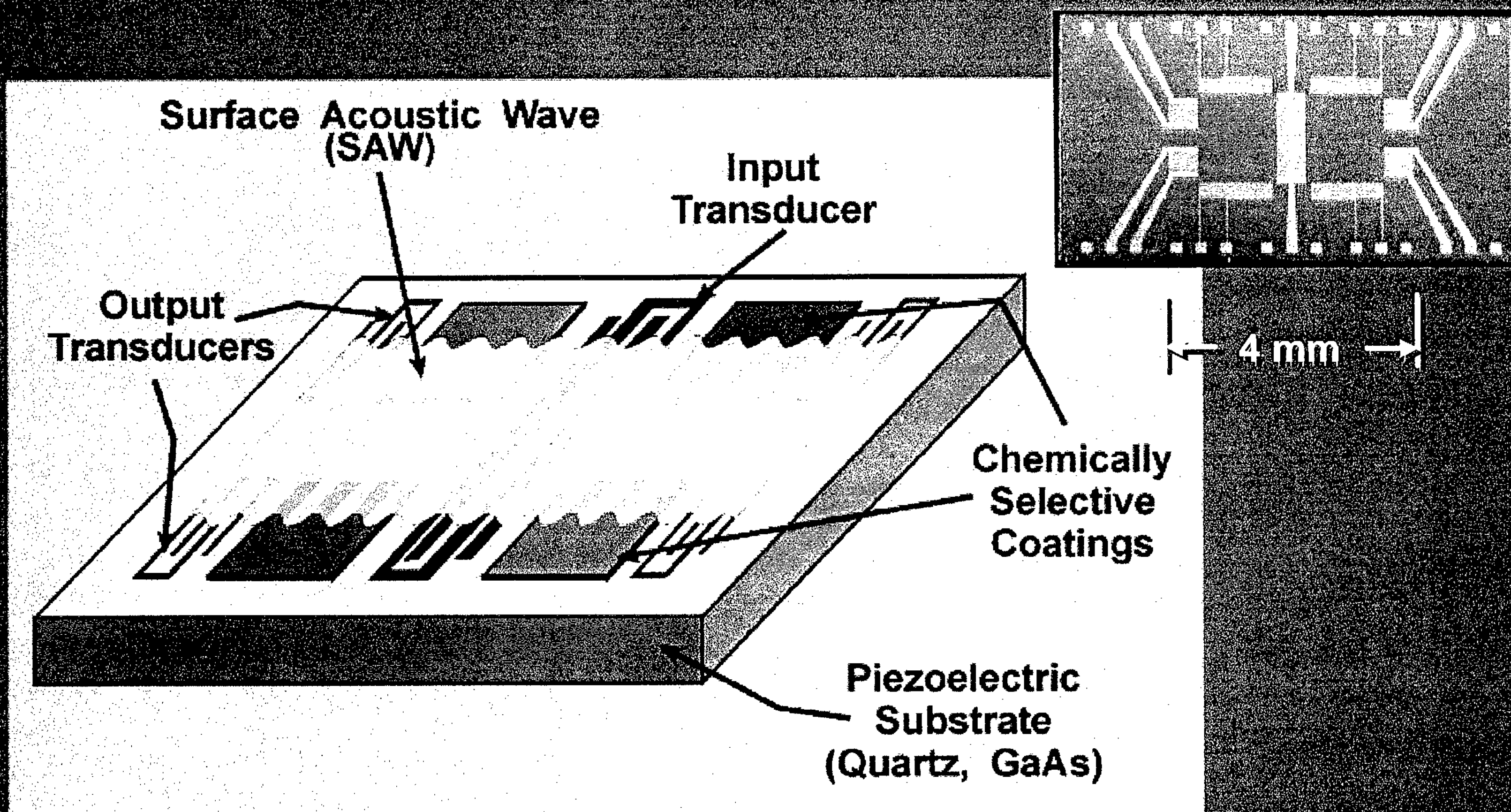
Surface Acoustic Wave Chemical Sensor Array

Purpose: To provide sensitive detection of analytes and interferant rejection.



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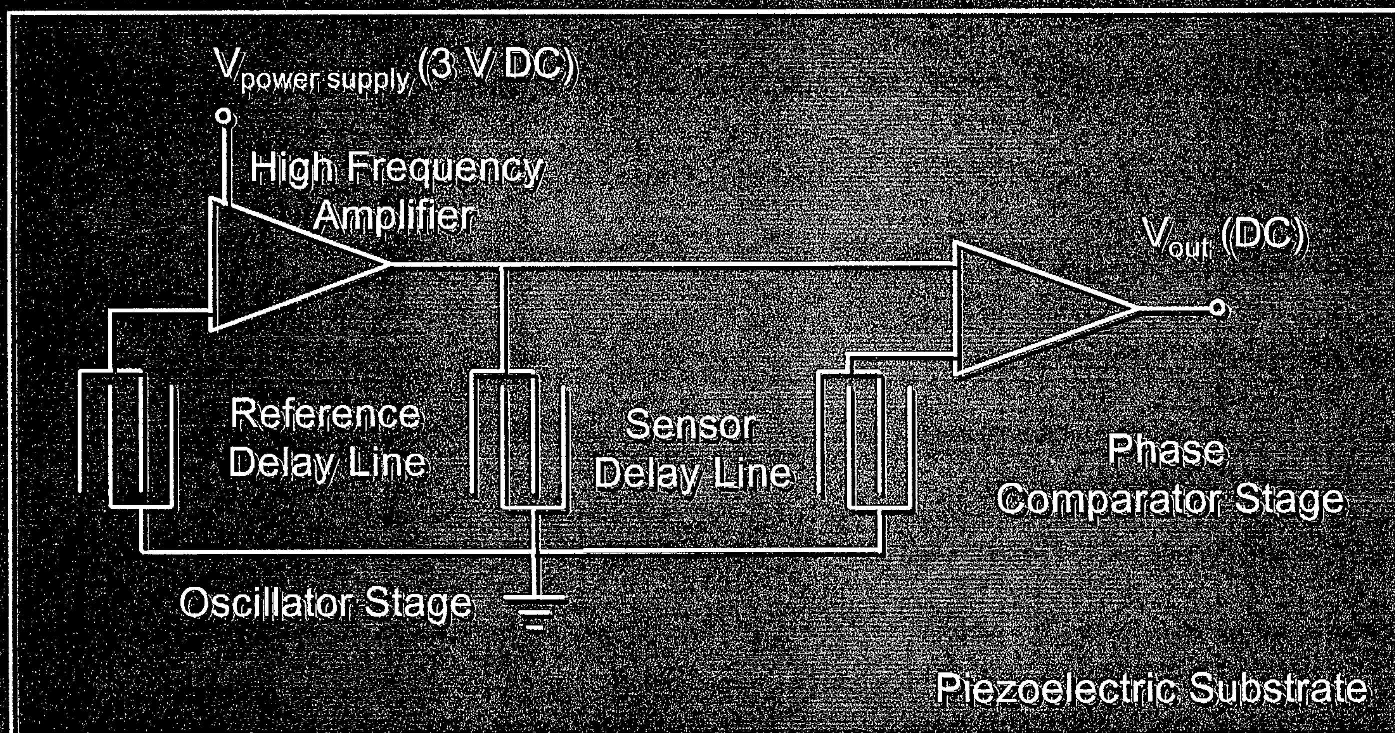
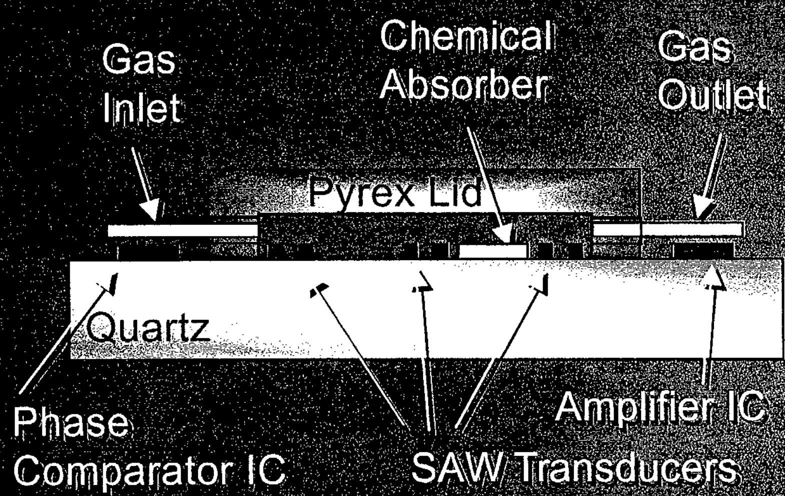
SAW Sensors Require RF (100 MHz - 1 GHz) Circuitry for Operation

Design: RF reference oscillator and phase comparator provide DC sensor readout.

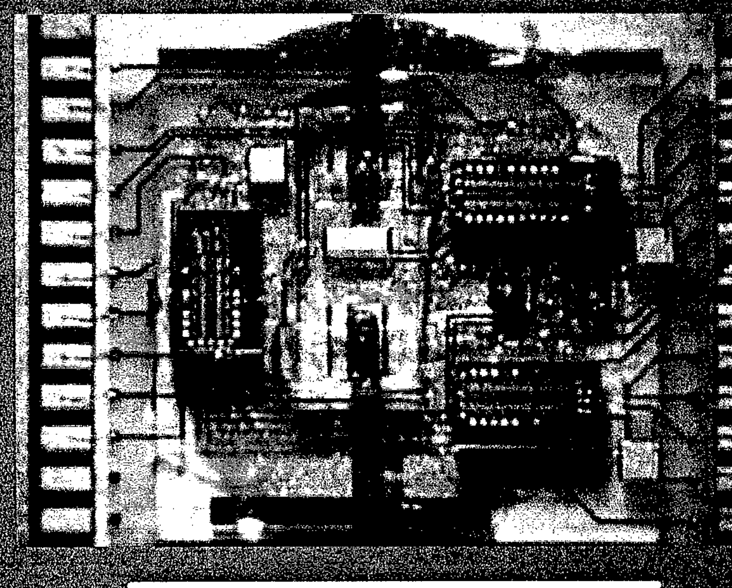


Quartz SAW Array / GaAs IC Hybrid Assembly

Fabrication: SAW sensor array and wiring traces are photolithographically produced on quartz substrate. GaAs ICs are wire-bonded directly to quartz substrate.



Cross Section



- DC in/out at quartz substrate
- 3-sensor array draws 90 mA @ 2.5 VDC

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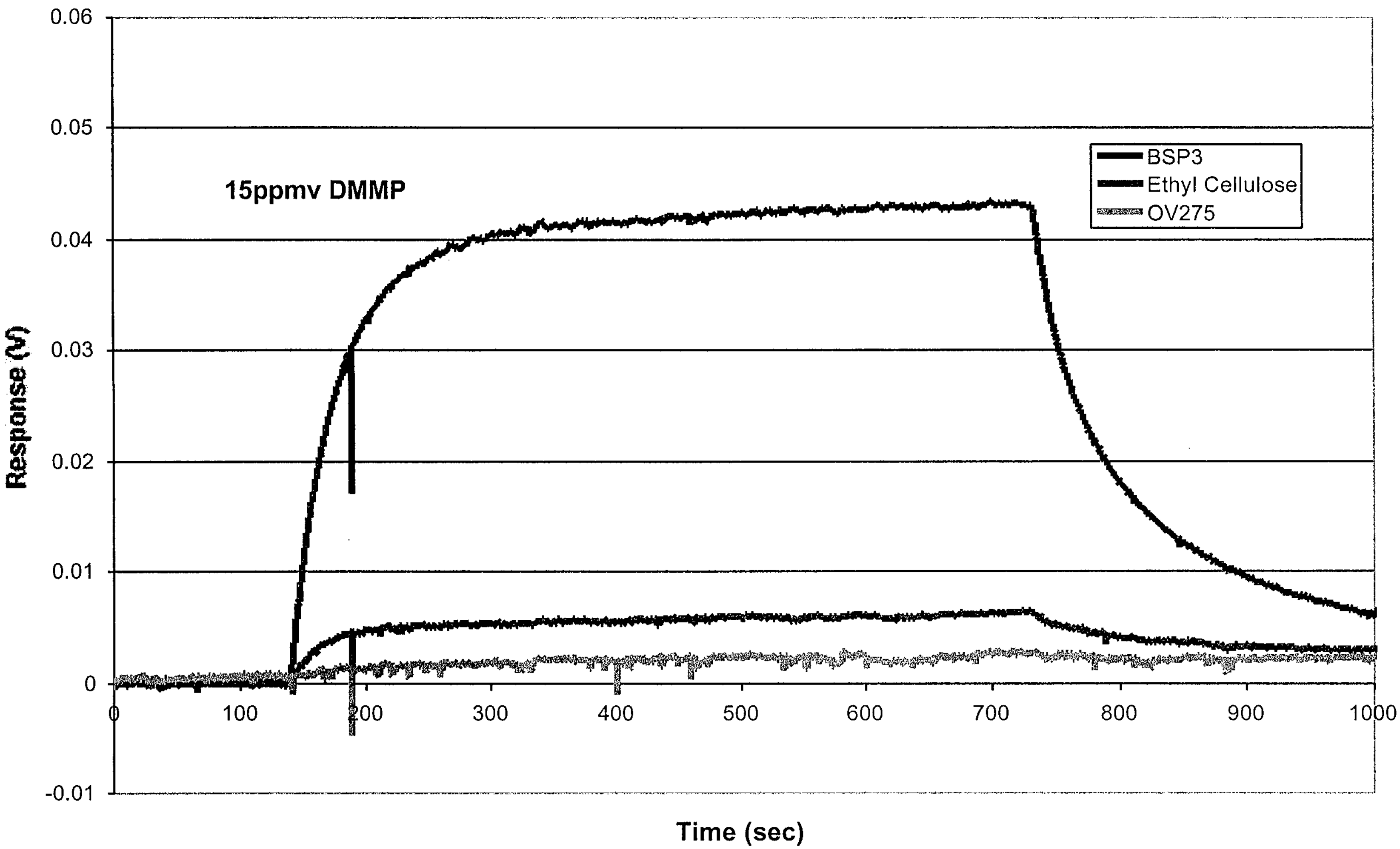
Hybrid SAW Array DMMP Response



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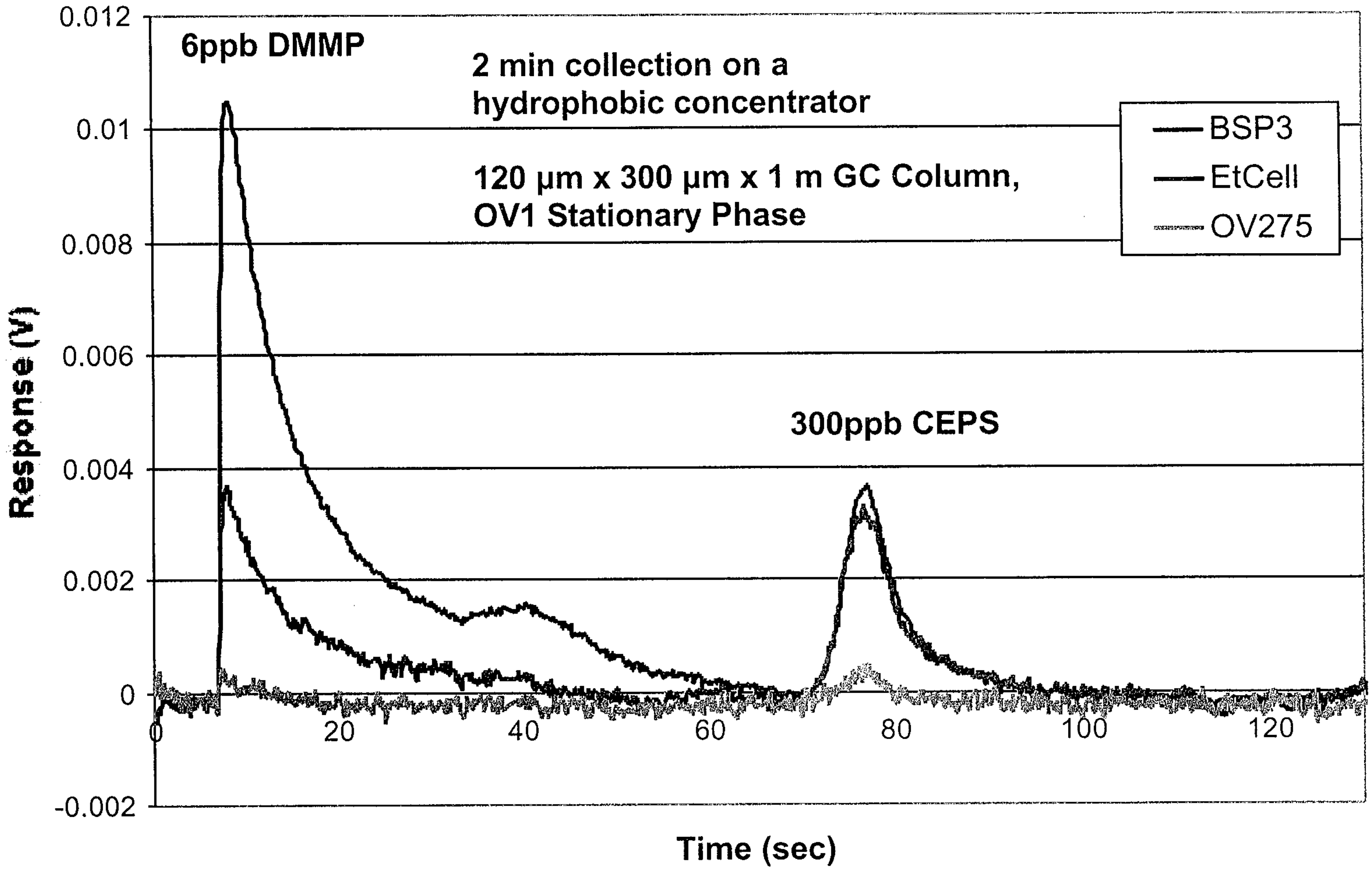
Concentrator + GC Column + Hybrid SAW Array: Chemical Response



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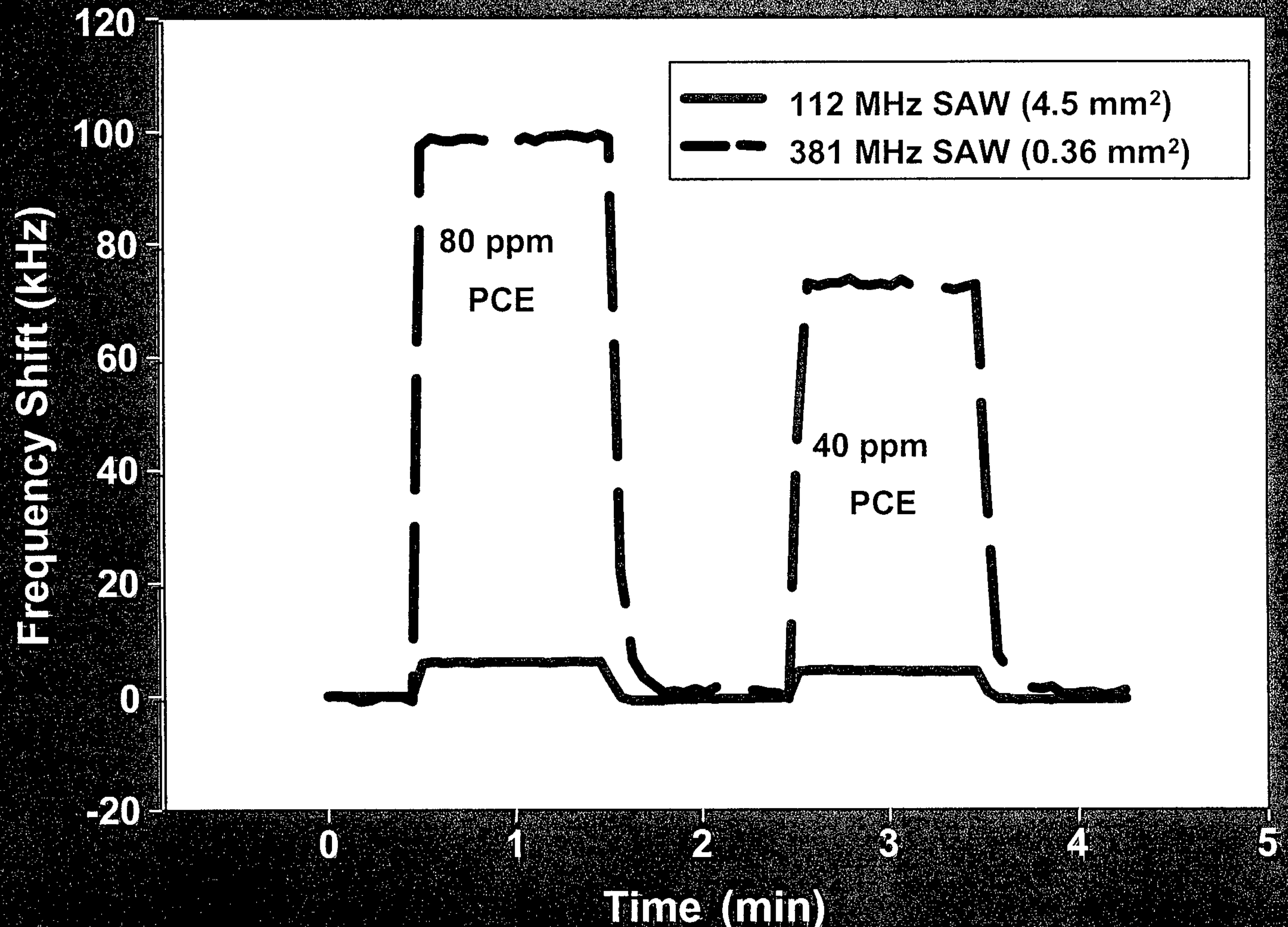
What I Havent Discussed:

- Packaging
- Liquid Phase Chemical Detection
- Pattern Recognition Algorithm for Data Analysis
- System Architecture

Where Its Going

- Temperature Control for Concentrator, Column, and SAW Array
- Higher Frequency Integrated SAW Detectors for Improved Sensitivity

Increasing SAW Frequency Provides Dramatic Decrease in Size and Increase in Sensitivity

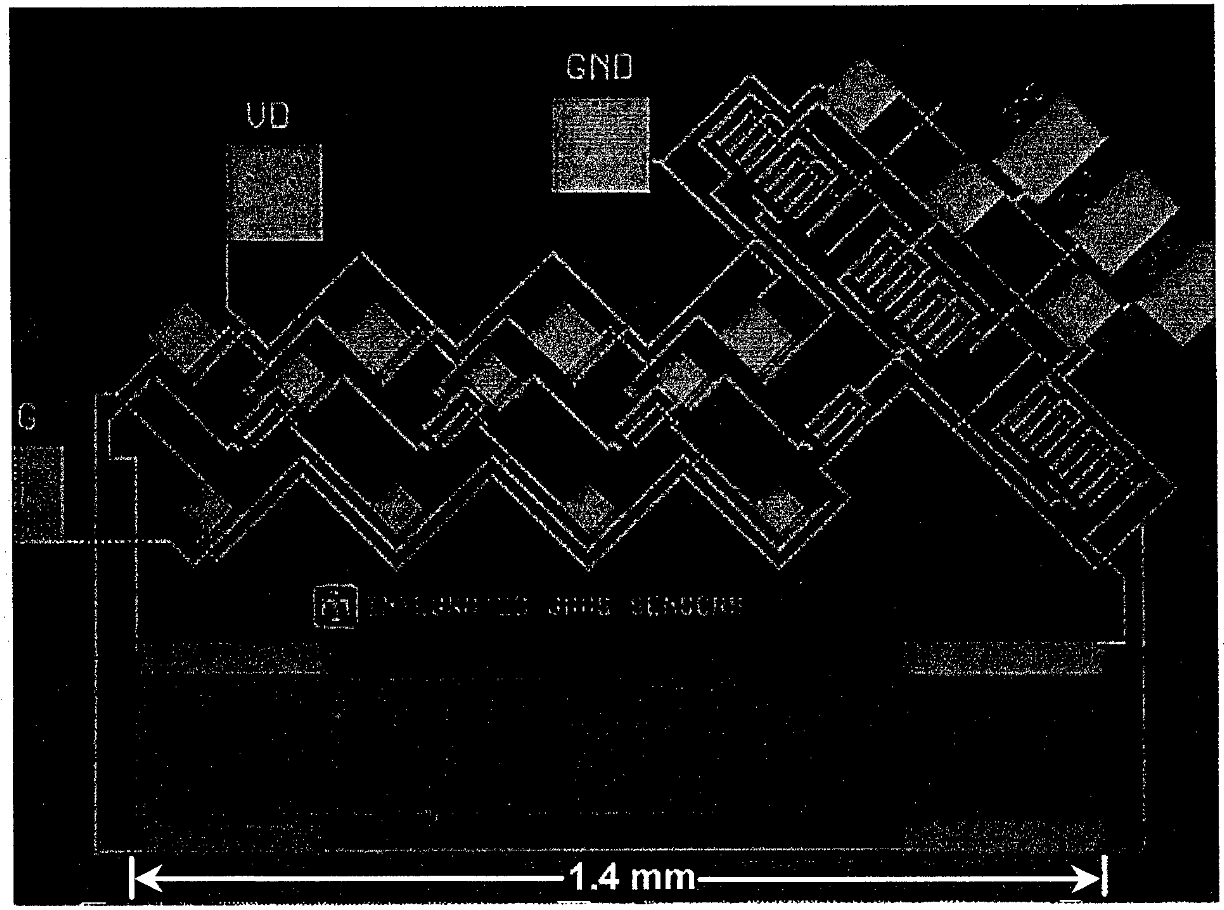


Integrated GaAs SAW Sensors and Drive Electronics

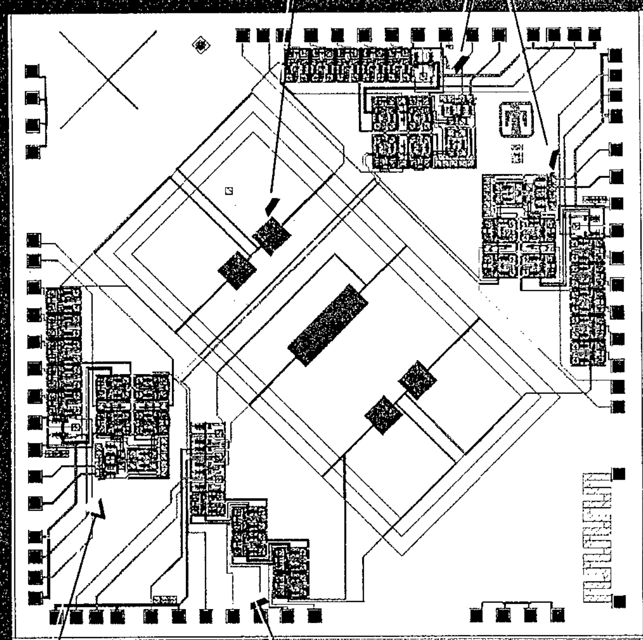
Design Goal: Single Chip, DC in/DC out, 4-Element Array

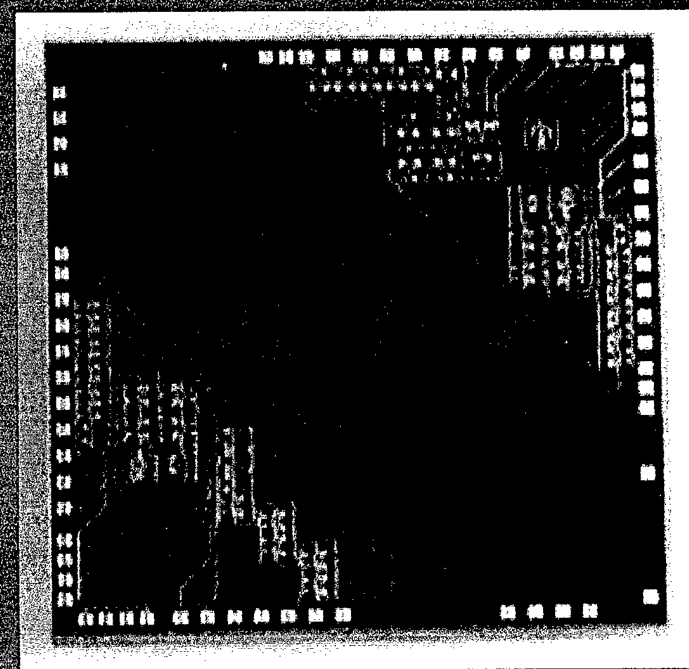
Oscillator Amplifier

470 MHz SAW Delay Line



Integrated DC In/DC Out GaAs SAW Delay Line Sensor





- GaAs foundry does not have "sensor" process
- SAW delay lines are post-processed in CSRL

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Speculation (in lieu of conclusion):

- Gas phase µreactors might employ µChemLab™ components
  - Preloaded "concentrators" as thermally activated reagent source
  - Concentrator cavity as reaction chamber with thermal sensor on membrane
  - Concentrator as µcalorimeter
  - SAW sensors with reactive coatings to monitor the progress of specific reactions

Microchemical Systems Development at DuPont

An Overview of the past 10 years

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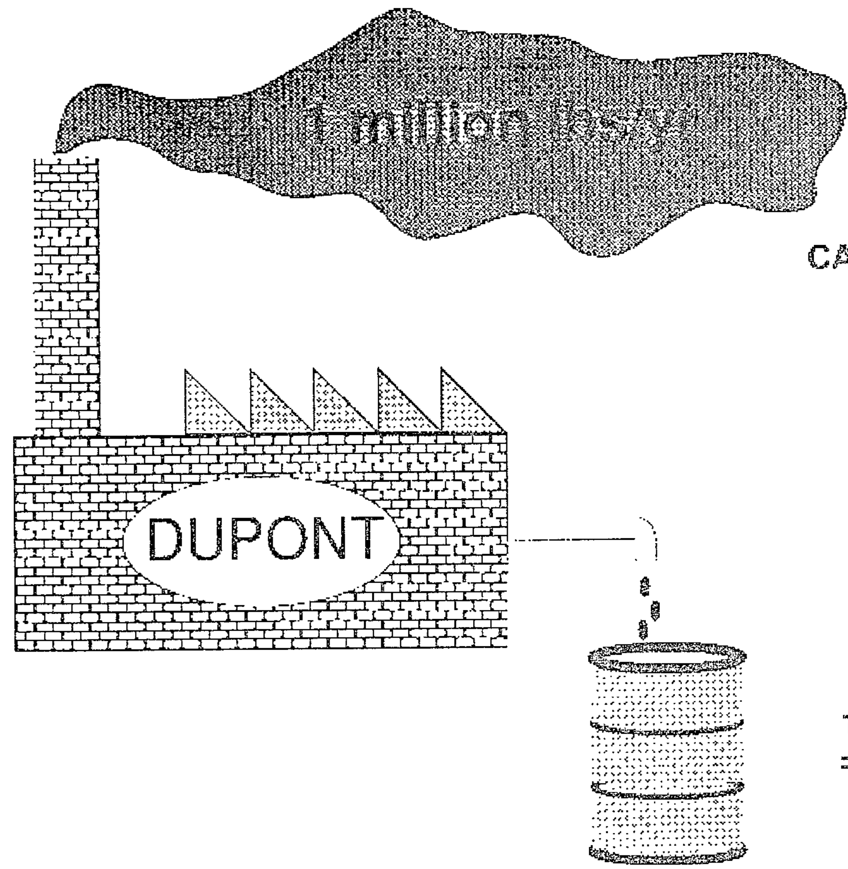
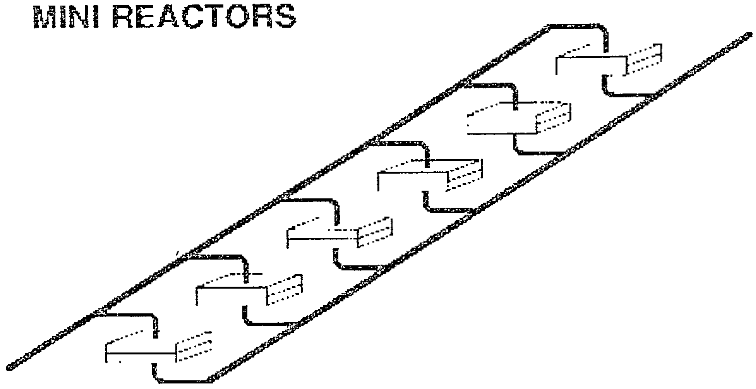


CAMPAIGNED PLANT

1 wk production
= 13 gpm

VS.

CONTINUOUS FLOW
MINI REACTORS



1 yr production
= .01 gpm per
mini reactor
(20 reactors)

Commercial Potential For Minichemical Systems

- Shorter Cycle Time from Lab to Commercial Production (scale-out)
- Phased Startup
- Distributed Manufacturing
- Better Control over Product Distribution
- Safer Operation
- *Wide Range of Materials of Construction*

Microchemical Systems Development at DuPont

- Late 80's -> '94 DuPont
- '94 - '97 DuPont Funded Collaboration with MIT
- '97 -> Pres. DARPA/DuPont Funded Collaboration with MIT

Microchemical Systems at DuPont

- Initial Applications - Hazardous Chemicals
- Enhanced Performance
- Analytical/Discovery Tools
- Complete Systems

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MINICHEMICAL SYSTEMS

Minichemical systems were designed and microfabricated for several candidate chemical processes. Preliminary experiments demonstrated technical feasibility, materials compatibility, thermal control, and safe operation.

REACTION CATEGORIES:

MINICHEMICAL SYSTEM CANDIDATES	FAST	CATALYTIC	PHOTOCHEMICAL	HIGH TEMPERATURE	HAZARDOUS
CYCLOHEXYL ISOCYANATE	X	X			X
HYDROGEN CHLORIDE OXIDATION		X			X
PHOSGENE	X	X			X
METHYL ISOCYANATE	X	X		X	X
HYDROGEN CYANIDE	X	X		X	X
DICHLORODIMETHYLSILANE CHLORINATION			X		X

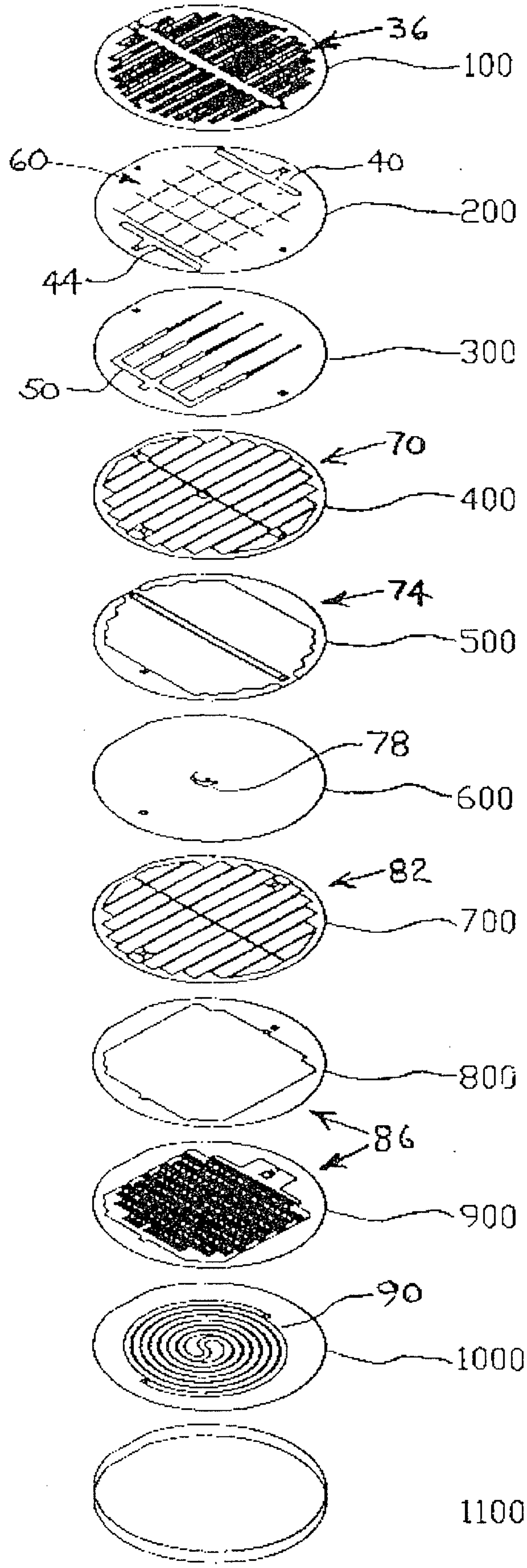
36
100
60
40
200
44
300
50
70
400
74
500
78
600
82
700
800
86
900
90
1000
1100

FIG. 3

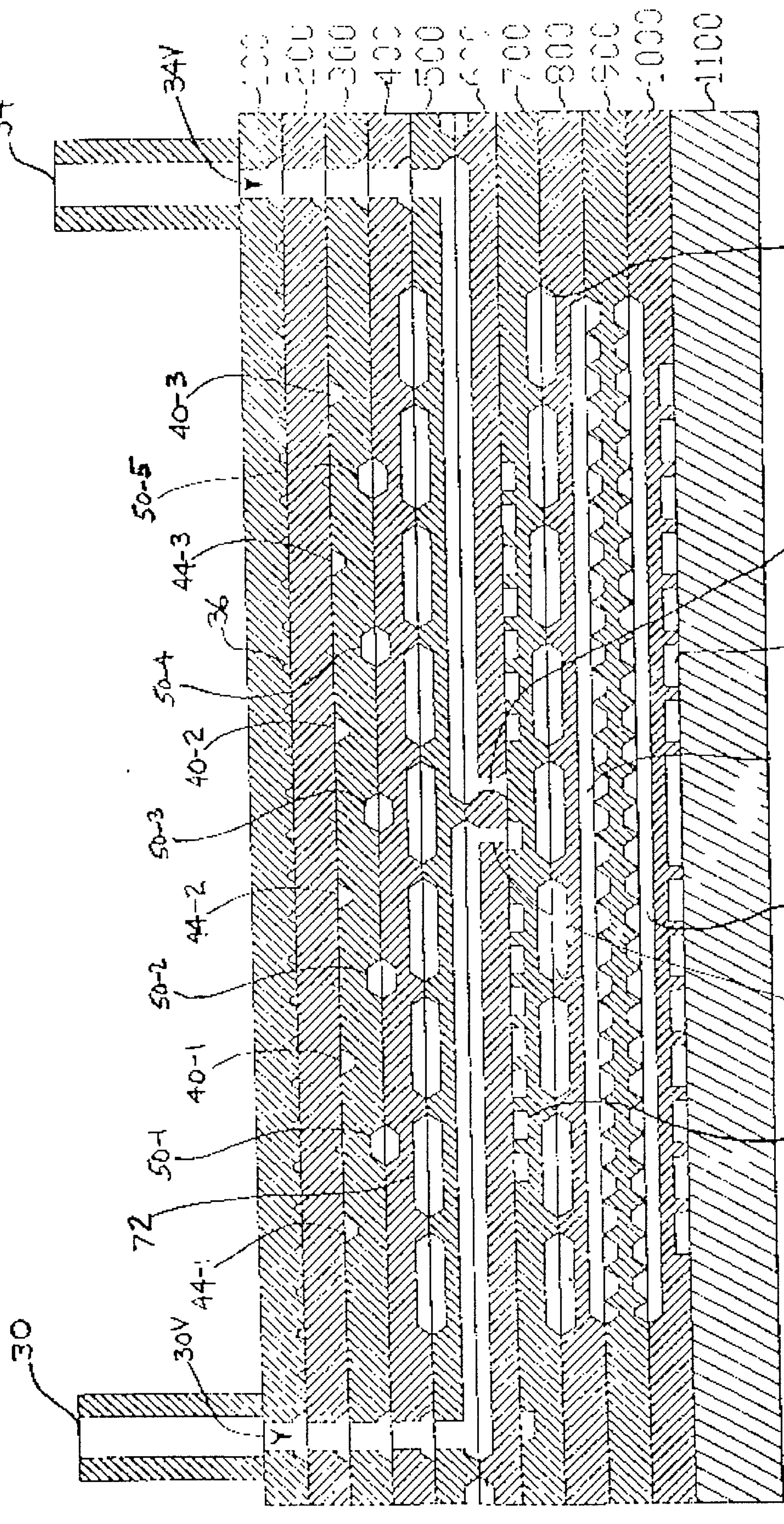
34
34V
100
200
300
400
500
600
700
800
900
1000
1100
82
40-3
50-5
44-3
36
50-4
40-2
50-3
44-2
50-2
40-1
50-1
72
44-1
30
30V
78V-2
90
87
88
78V-1
78

FIG 4

Butyl Isocyanate

- $(C_4H_9)\text{-}NH_2 + COCl_2 \longrightarrow (C_4H_9)\text{-}N{=}C{=}O + 2HCl$

» Main Side Reaction

- $(C_4H_9)\text{-}NH_2 + HCl \longleftrightarrow (C_4H_9)\text{-}NH_2\text{-}HCl$

  - Very Fast
    - Run in solvent to reduce overall rate
    - Typical process yields are ~70%
      - » 10-30 lbs waste per 100 lbs product

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Butyl Isocyanate

- Gas Phase Reaction
  - Rapid Mixing -> Reduced Byproduct Formation
  - Side Reaction between BA and HCl Suppressed
  - Potentially Explosive
- Microreactor
  - Potential for Isothermal Operation and Rapid Mixing

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Butyl Isocyanate

- Characteristic Results
  - Run A
    - Phosgene/BA: 1.2
    - Temperature 325 C
    - Yield 91.6%
  - Run B
    - Phosgene/BA 1.8
    - Temperature 300 C
    - Yield 97.3

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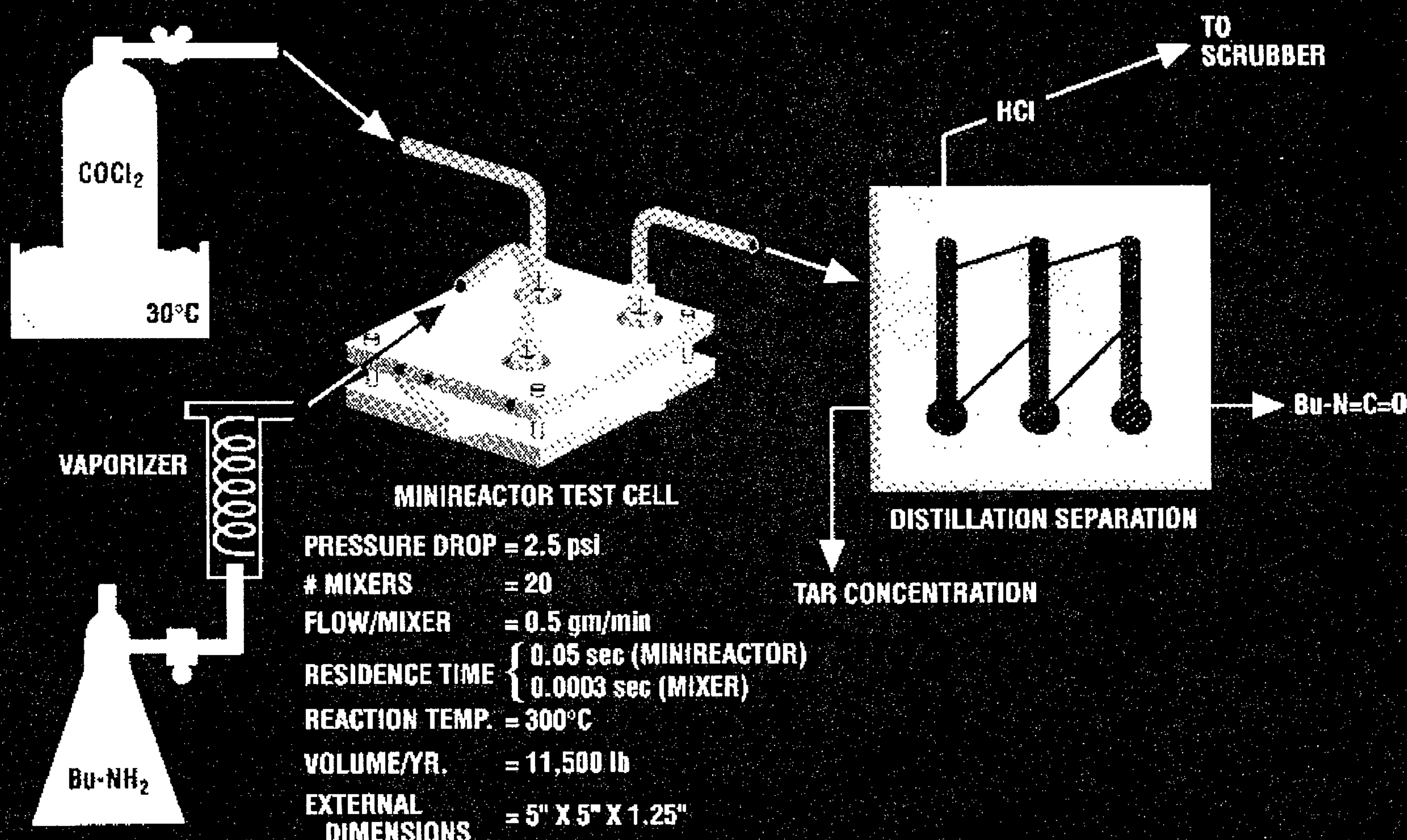
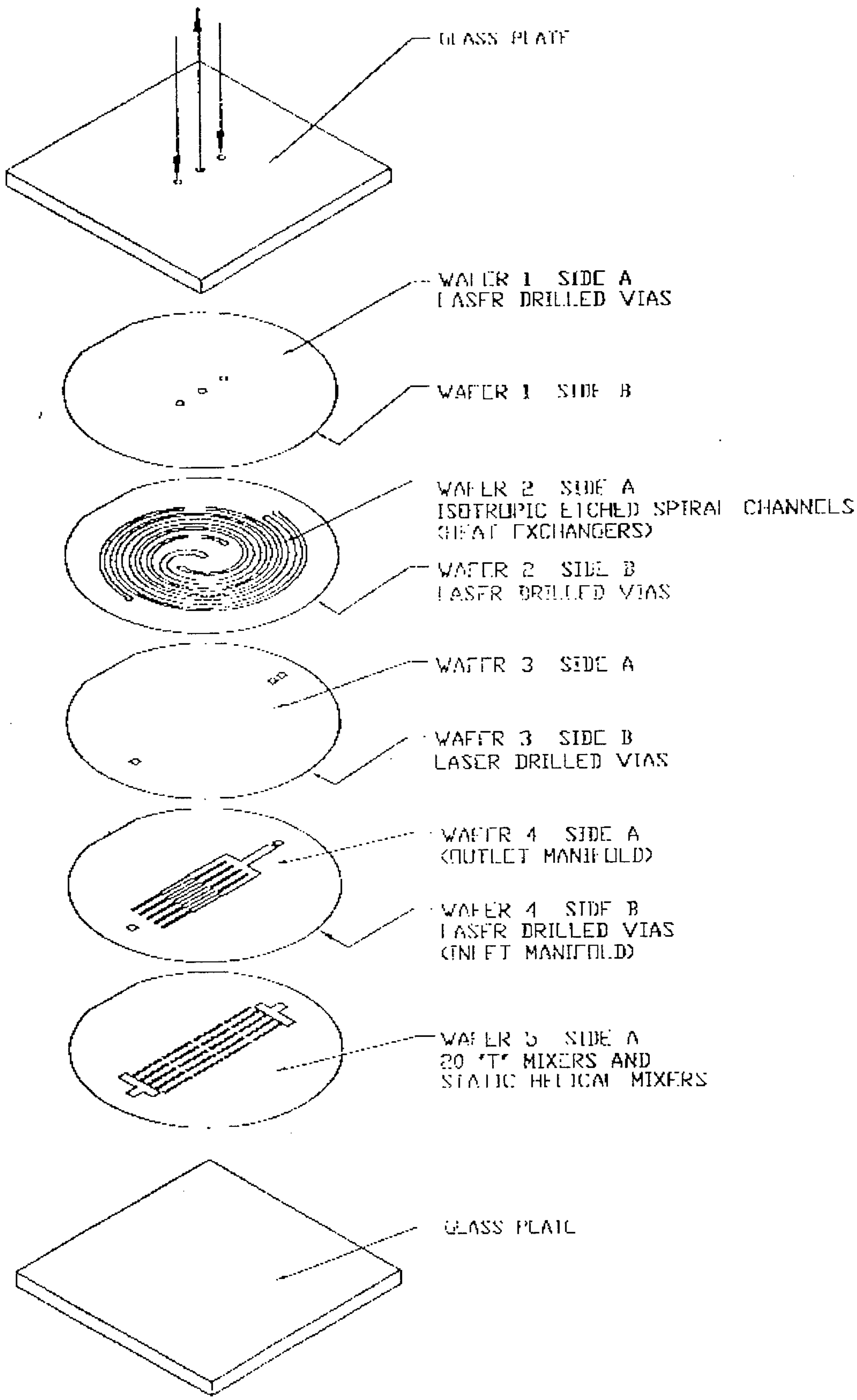
Butyl Isocyanate Vapor Phase Reaction System



PRESSURE DROP = 2.5 psi
MIXERS = 20
FLOW/MIXER = 0.5 gm/min
RESIDENCE TIME { 0.05 sec (MINIREACTOR) / 0.0003 sec (MIXER)
REACTION TEMP. = 300°C
VOLUME/YR. = 11,500 lb
EXTERNAL DIMENSIONS = 5" X 5" X 1.25"


GLASS PLATE
WAFER 1 SIDE A
LASER DRILLED VIAS
WAFER 1 SIDE B
WAFER 2 SIDE A
ISOTROPIC ETCHED SPIRAL CHANNELS
(HEAT EXCHANGERS)
WAFER 2 SIDE B
LASER DRILLED VIAS
WAFER 3 SIDE A
WAFER 3 SIDE B
LASER DRILLED VIAS
WAFER 4 SIDE A
(OUTLET MANIFOLD)
WAFER 4 SIDE B
LASER DRILLED VIAS
(INLET MANIFOLD)
WAFER 5 SIDE A
20 "T" MIXERS AND
STATIC HELICAL MIXERS
GLASS PLATE

B1

Methyl Isocyanate

- $CH_3NHCHO + 0.5\ O_2 \longrightarrow CH_3NCO + H_2O$

  – Notable Side Reactions:

  – Decomposition of MMF to MA
    - $CH_3NHCHO \longleftrightarrow CH_3NH_2 + CO$

  – Oxidation of MA
    - $CH_3NH_2 + 1.5\ O_2 \longrightarrow NH_3 + CO_2 + H_2O$

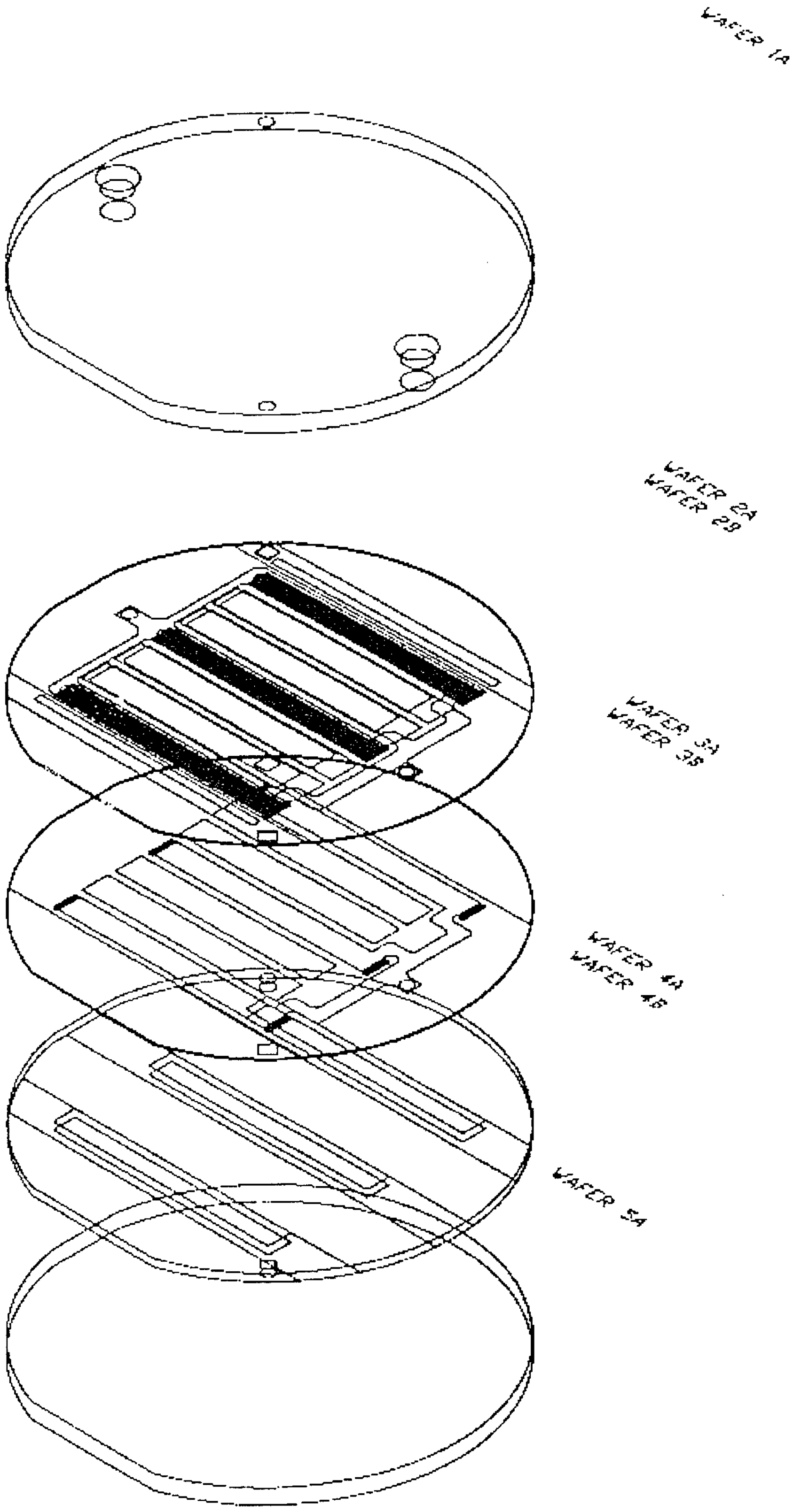
  – Oxidation of Ammonia and Carbon Monoxide

DUPONT

Methyl Isocyanate

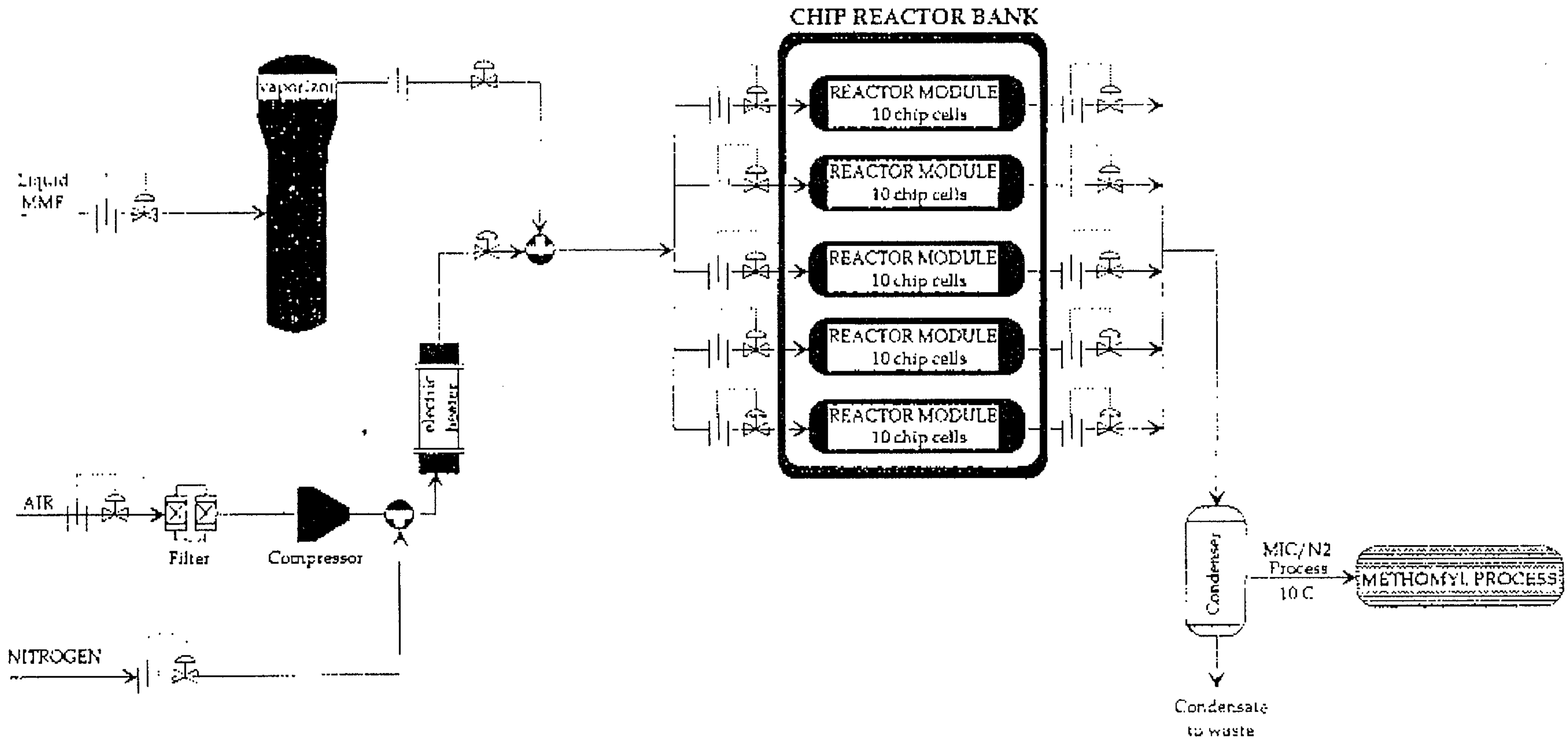
- Highly Exothermic (~50 kcal/mole MMF)
- Very Fast
- Relatively High Temp. (500 - 650 C)
- Peak Temperature limited by melting point of catalyst
- Highly Toxic - consume as produced
- 2-stage Adiabatic Reactor

DUPONT


WAFER 1A
WAFER 2A
WAFER 2B
WAFER 3A
WAFER 3B
WAFER 4A
WAFER 4B
WAFER 5A

AUG 10 1992

Chip Reactors - MIC Process



DUPONT
ENGINEERING DEPARTMENT
Cheri I. Thomas
13 January 1992

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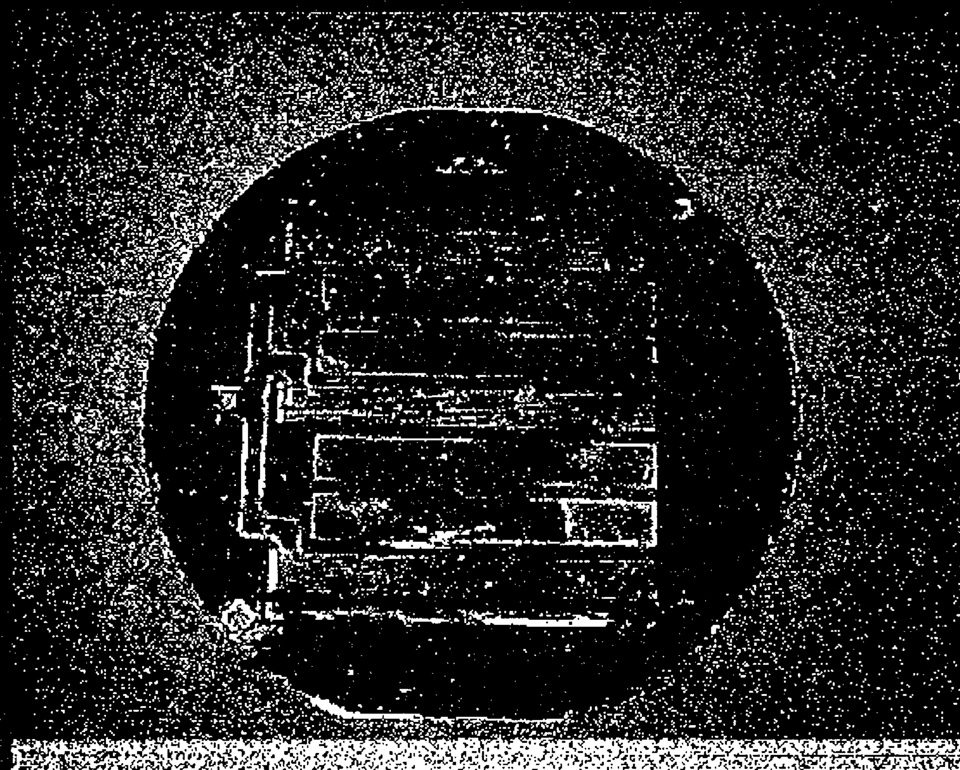
Methy Isocyanate Single Stage Microreactor



Methyl Isocyanate

- Standard Plant (2-stage)
  - Overall Conversion of MMF 95-100%
  - Overall Process Yield 70-75%
- Microreactor (Single Stage)
  - Conversion 85-95%
  - Selectivity down 5%
- Implication: Microreactor Should Also Be Multistage

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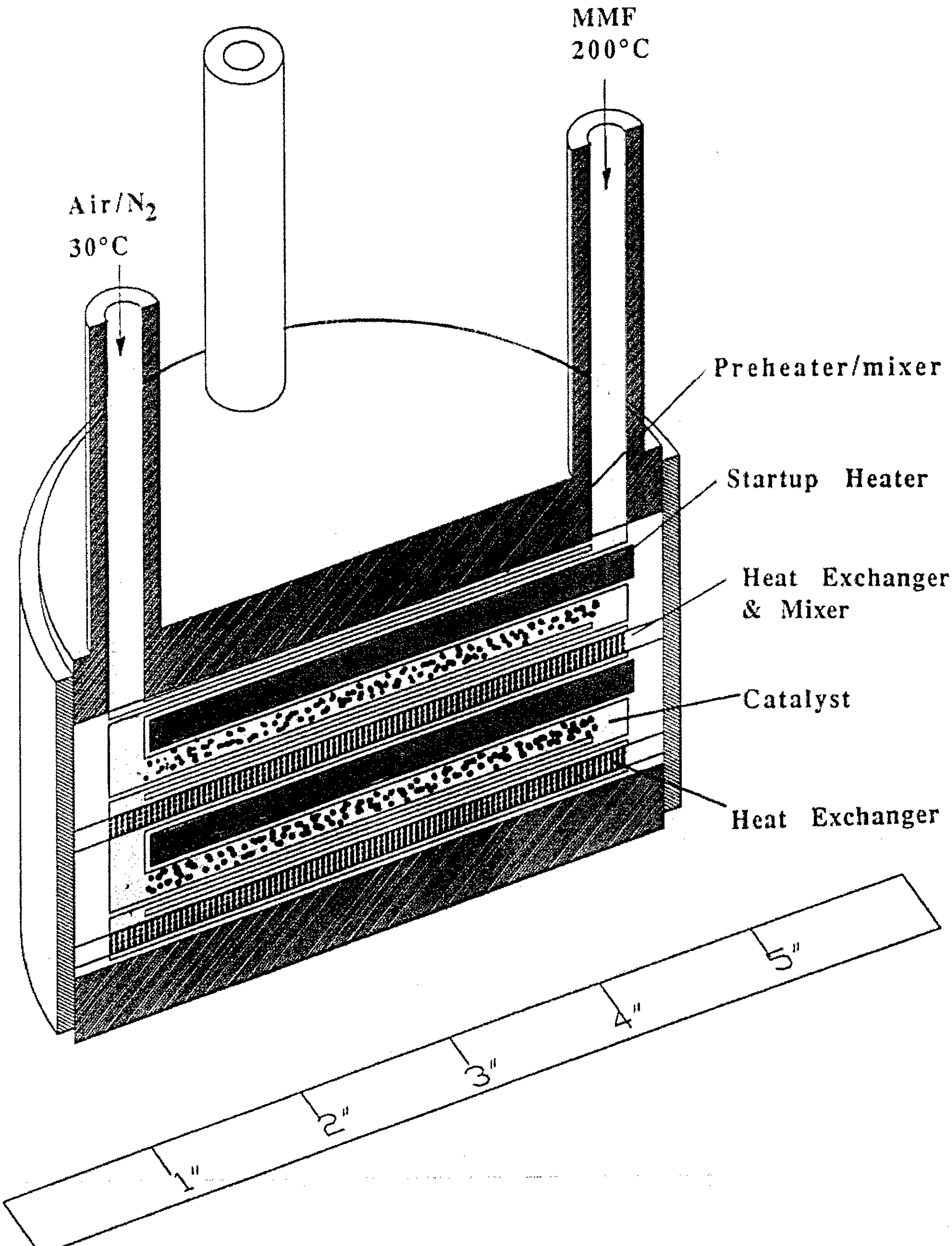
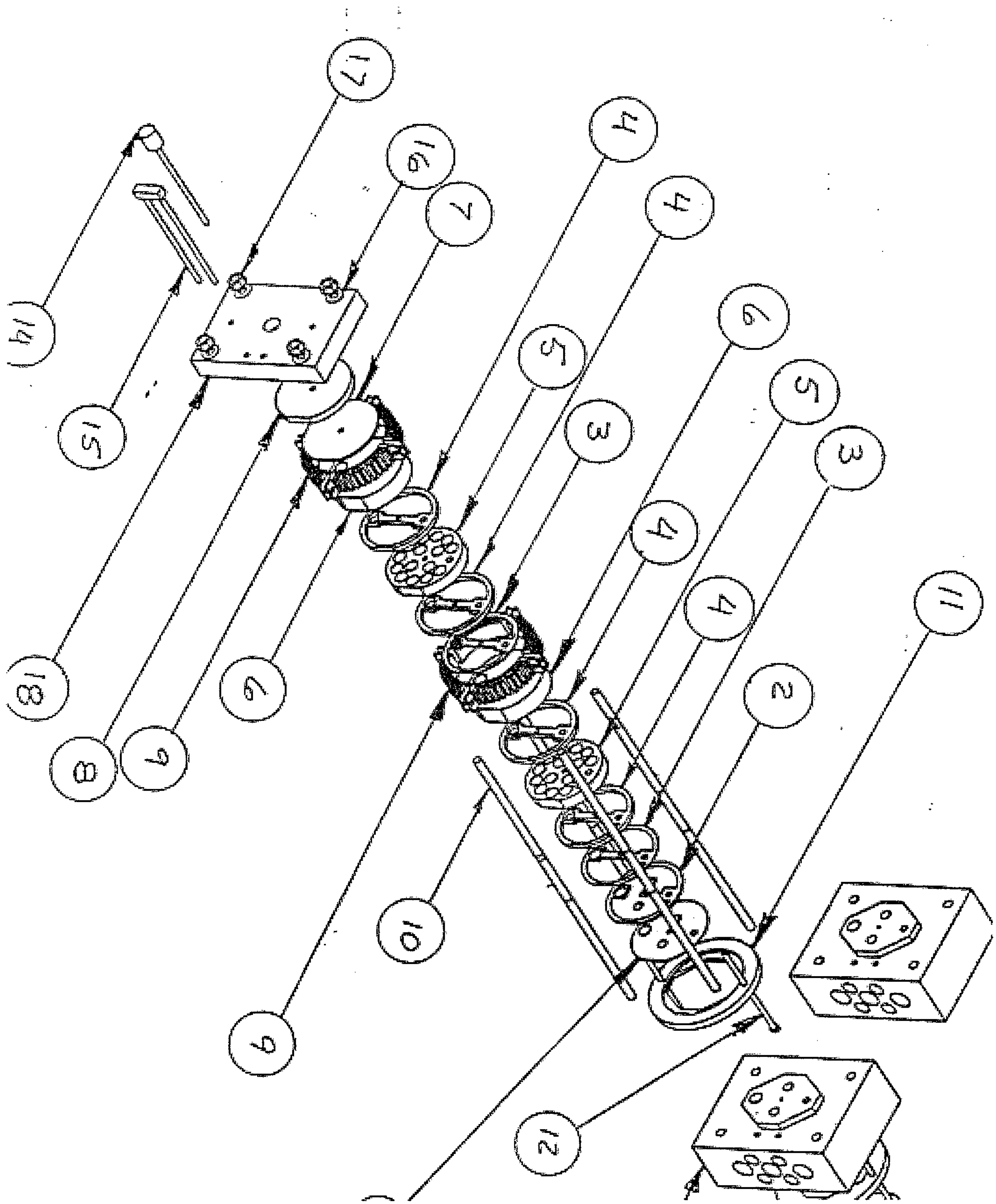
SUMMARY OF MINIREACTOR RESULTS

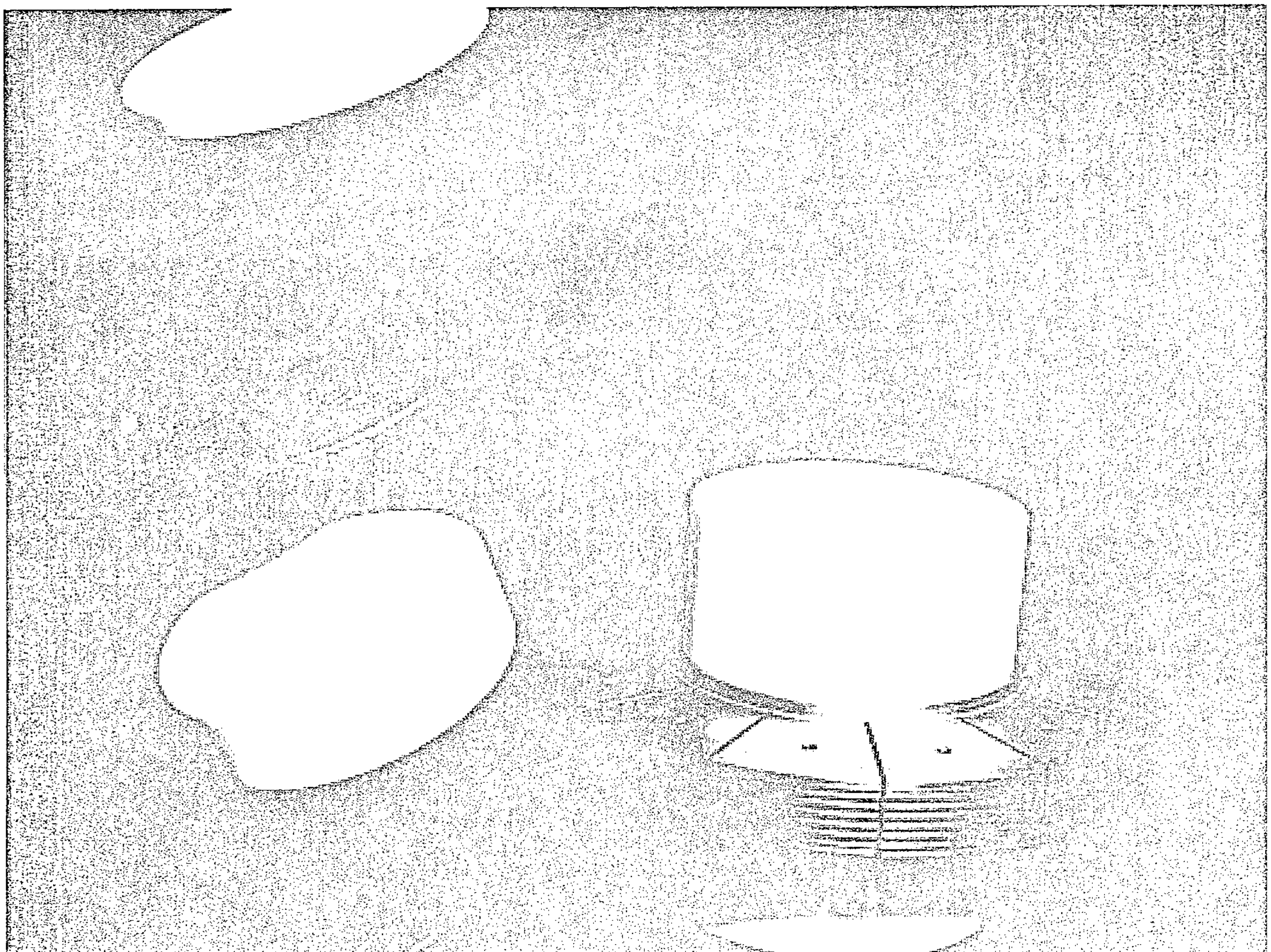
CASE NO.	CELL NO.	MMF RATE g/min	O_2 EXCESS %	Rx TEMP., °C			PC VENT AREA %			MMF CONV. %
				PH	HTR.	EXIT	CO_2	MIC	CO	
1	1	0.64	33	419	530	521	4.3	25.0	1.9	97
2	2	0.8	6	410	530	523	2.3	32.3	-	91
3	2	0.8	6	382	480	474	2.2	31.1	-	85
4	2	1.6	6	377	530	525	2.3	31.5	-	93
5	3*	1.6	6	305	530	485	2.3	31.3	-	87
6	3*	1.6	6	329	600	545	2.8	31.4	-	91
7	3*	1.6	6	344	650	588	3.0	30.6	-	93
8	4*	0.8	6	329	530	466	2.5	32.5	-	91
"NORMAL"		1.6	6	-	-	-	2.2	33.3	0.4	99

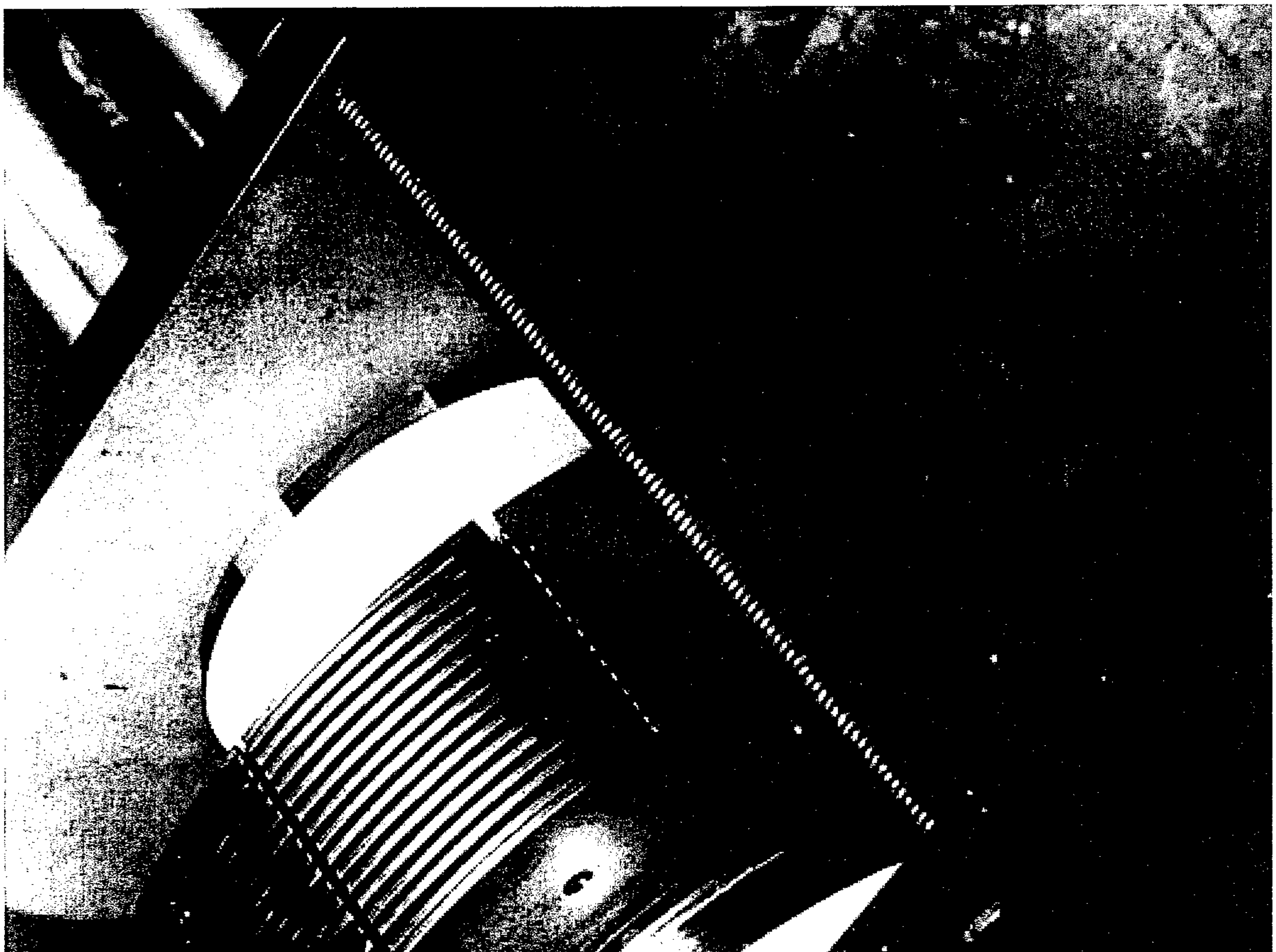
* LOCATION CHANGED FOR PREHEAT AND REACTOR TC'S DUE TO FITTING CHANGE. TC'S ABOUT 1/2 INCH FURTHER FROM CELL

MIC COMMERCIAL CELL CONCEPT A

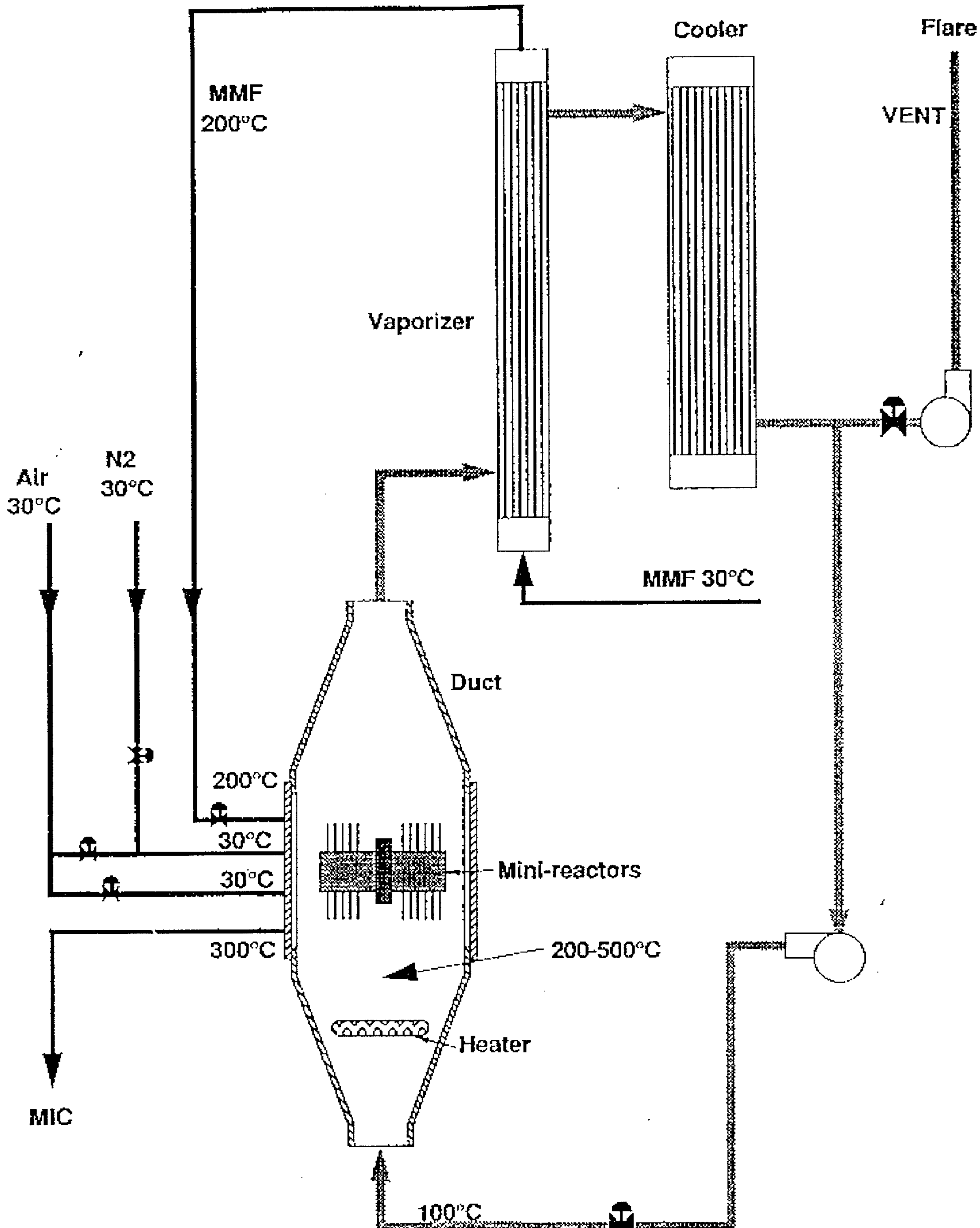








MIC HOT GAS SYSTEM CONCEPT



8/11/93

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HCN and TFE

- Very High Temperature
- Materials of Construction Issues
- Transport Regulated

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OBJECTIVE: DEVELOPMENT OF MICROSCALE REACTOR FOR ON-SITE GENERATION OF HCN FOR SMALL VOLUME APPLICATIONS SUCH AS DYE MANUFACTURING, VITAMIN AND DRUG PRODUCTION, ETC. HYDROGEN CYANIDE IS COMMERCIALLY PRODUCED VIA ONE OF TWO ROUTES: THE DEGUSSA AND ANDRUSSOW PROCESSES. WHILE THE ANDRUSSOW PROCESS IS ECONOMICAL FOR LARGE SCALE PRODUCTION, THE YIELD OF HCN IS LOW REQUIRING EXTENSIVE PURIFICATION STEPS. THE DEGUSSA PROCESS PROVIDES HIGHER YIELDS OF HCN AND USABLE BY-PRODUCT HYDROGEN, BUT COST OF THE PT COATED CERAMIC TUBES IS HIGH, HEAT TRANSFER EFFICIENCY IS LIMITED, AND THE RISK ASSOCIATED WITH THERMAL STRESS OF EXPENSIVE CERAMIC COMPONENTS IS FORMIDABLE. THE PRODUCTION OF HCN FROM A SINGLE FEED SUCH AS METHYLAMINE OR FORMAMIDE MIGHT PROVIDE, FROM A FLOW CONTROL, SEPARATION, AND THERMAL STANDPOINT, A RELATIVELY SIMPLE SOLUTION.

ANDRUSSOW PROCESS

$$CH_4 + NH_3 + 3/2\,O_2 \longrightarrow HCN + 3H_2O$$

$$\Delta H = -114 \text{ KCAL/GMOL}$$

DEGUSSA PROCESS

$$NH_3 + CH_4 \longrightarrow HCN + 3H_2$$

$$\Delta H = +60 \text{ KCAL/GMOL}$$

METHYLAMINE DECOMPOSITION

$$CH_3NH_2 \longrightarrow HCN + 2H_2$$

$$\Delta H = +38 \text{ KCAL/GMOL}$$

accounts for virtually all (>95%) of the methylamine reacted

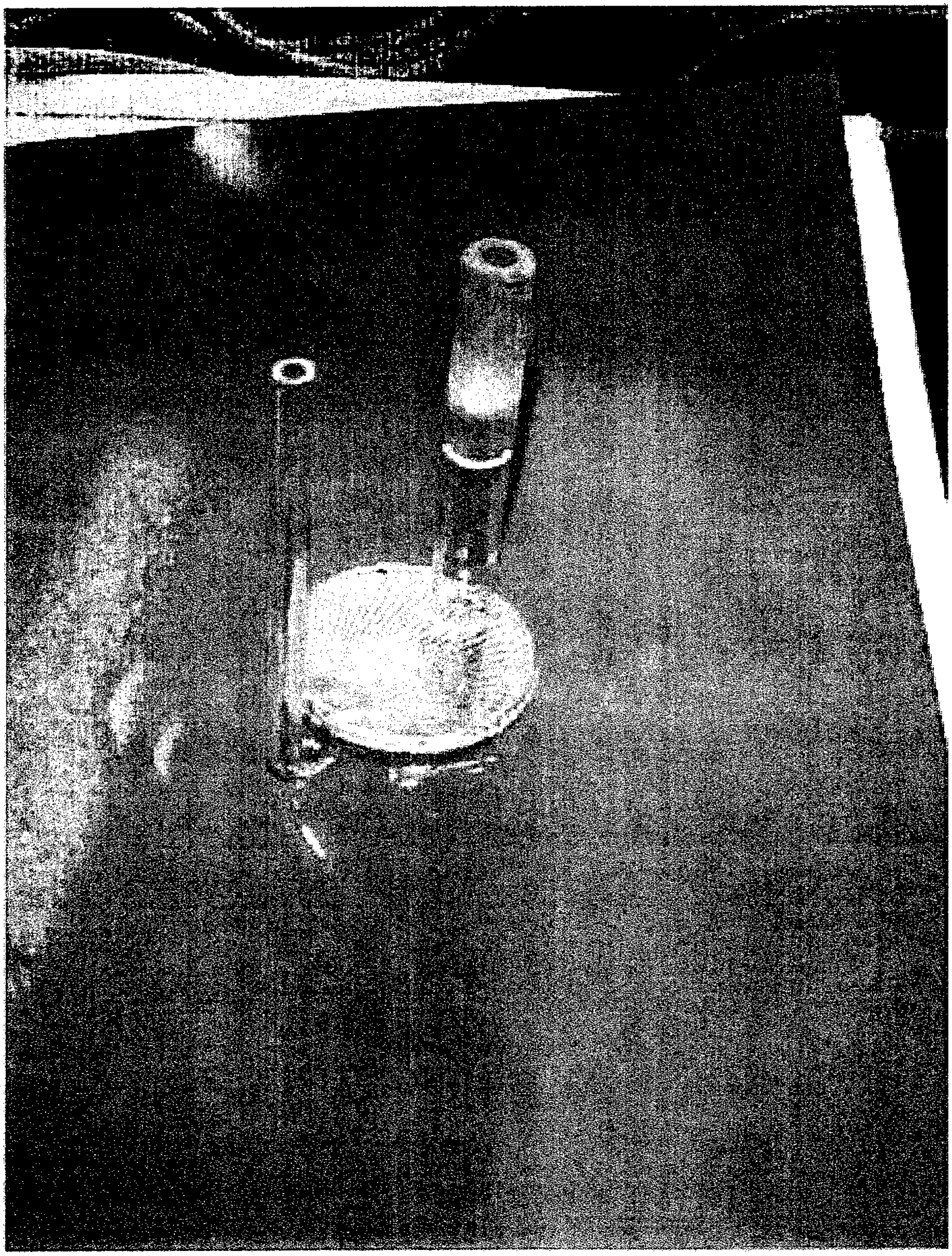
Synthesis of HCN from Monomethylamine Using Thermal Heating

Catalyst: 90/10 Pt/Rh Gauze
Reactor Location: At the top of heating zone

Obs. No.	MMA (sccm)	N2 (sccm)	Total (sccm)	Res. Time (s)	React Press psig	React Temp (C)	GC psig	Conv (%) CH4	Sel (%) HCN	Yield (%) HCN
1	17.8	0	17.8	1.0	1.0	955	1.0	100.0	81.0	81.0
2	18.6	0	18.6	1.0	1.0	955	1.0	100.0	81.0	81.0
3	17.0	0	17.0	1.1	1.0	955	1.0	100.0	81.0	31.0
4	35.6	0	35.6	0.5	1.0	955	1.0	100.0	88.9	88.9
5	35.6	0	35.6	0.5	1.0	955	1.0	100.0	88.4	88.4
6	35.6	0	35.6	0.5	1.0	955	1.0	100.0	88.4	88.4
7	35.6	0	35.6	0.5	1.0	954	1.0	100.0	88.5	88.5
8	37.2	0	37.2	0.5	1.0	955	1.0	100.0	88.6	88.6
9	36.4	0	36.4	0.5	1.0	954	1.0	100.0	88.7	88.7
10	35.6	0	35.6	0.5	1.0	955	1.0	100.0	88.8	88.8
11	36.4	0	36.4	0.5	1.0	954	1.0	100.0	88.8	88.8
12	43.6	0	43.6	0.4	1.0	954	1.0	100.0	88.2	88.2
13	43.6	0	43.6	0.4	1.0	954	1.0	100.0	88.1	88.1
14	43.6	0	43.6	0.4	1.0	955	1.0	100.0	88.1	88.1
15	45.2	0	45.2	0.4	1.1	954	1.1	100.0	88.0	88.0
16	52.5	0	52.5	0.3	1.2	954	1.2	100.0	88.0	88.0
17	53.3	0	53.3	0.3	1.1	952	1.1	100.0	87.9	87.9
18	53.3	0	53.3	0.3	1.1	952	1.1	100.0	87.9	87.9
19	51.7	0	51.7	0.4	1.0	952	1.0	100.0	88.4	88.4
20	50.9	0	50.9	0.4	1.0	951	1.0	100.0	88.3	88.3
21	50.9	0	50.9	0.4	1.0	950	1.0	100.0	88.3	88.3
22	50.1	0	50.1	0.4	1.0	1051	1.0	100.0	82.2	82.2
23	51.7	0	51.7	0.4	1.0	1051	1.0	100.0	82.2	82.2
24	50.1	0	50.1	0.4	1.0	1051	1.0	100.0	82.1	82.1
25	49.3	0	49.3	0.4	1.0	1051	1.0	100.0	82.2	82.2
26	50.1	0	50.1	0.4	1.0	1051	1.0	100.0	82.2	82.2
27	50.9	0	50.9	0.4	1.0	1130	1.0	100.0	83.6	83.6
28	51.7	0	51.7	0.4	1.0	1123	1.0	100.0	82.8	82.8
29	50.9	0	50.9	0.4	1.0	1127	1.0	100.0	82.8	82.8
30	51.7	0	51.7	0.4	1.0	1128	1.0	100.0	83.0	83.0
31	52.5	0	52.5	0.3	1.0	905	1.0	100.0	88.4	88.4
32	53.3	0	53.3	0.3	1.0	905	1.0	100.0	88.2	88.2
33	53.3	0	53.3	0.3	1.0	904	1.0	100.0	88.2	88.2
34	53.3	0	53.3	0.3	1.0	856	1.0	100.0	84.6	84.6
35	53.3	0	53.3	0.3	1.0	855	1.0	100.0	84.1	84.1
36	53.3	0	53.3	0.3	1.0	855	1.0	100.0	83.6	83.6
37	53.3	0	53.3	0.3	1.0	813	1.0	100.0	72.1	72.1

Synthesis of HCN from Methane and Ammonia Using Induction Heatin

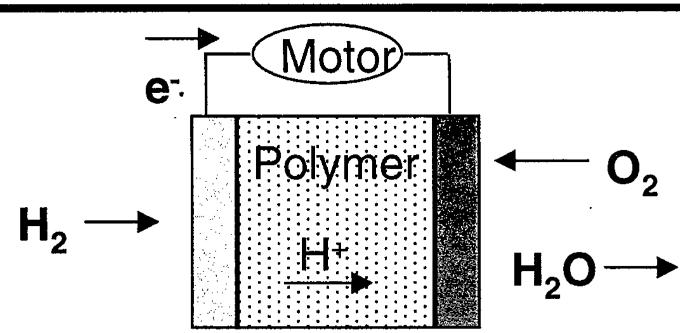
Run #	POWER (watts)	CH4(sccm)	NH3(sccm)	H2 (%)	N2 (%)	CH4 (%)	NH3 (%)	HCN (%)
1	230	16.4	15.2	0	0	44	53	0
2	230	16.4	15.2	0	0	39	59	0
3	230	16.7	15.2	0	0	39	58	0
4	230	16.4	15.2	0.1	0.9	39	56	0
5	230	16.4	15.2	43.1	10.1	17.6	15.7	15.0
6	235	16.4	15.2	64.6	7.4	0.8	2.1	20.1
7	230	17.1	15.2	64.2	7.1	2.6	20.2	22.8
8	230	16.7	15.2	62.2	7.0	2.1	4.2	20.1
9	230	17.1	15.2	64.6	7.1	0.0	2.6	20.8
10	240	18.1	15.2	65.3	6.1	0.0	1.7	22.5
11	240	19.2	15.2	65.2	5.7	0.0	1.8	22.6
12	240	17.4	15.2	42.4	13.0	5.1	20.3	3.1
13	235	17.1	15.2	54.3	7.3	7.1	8.0	18.2
14	250	17.7	15.2	62.4	7.2	0.0	2.6	20.4
15	250	18.4	15.2	54.5	6.8	7.9	7.4	22.8
16	270	20.7	15.2	61.7	7.1	0.0	1.6	23.0
17	275	22.4	15.2	64.0	5.6	0.6	0.4	24.1



Hydrocarbon Fuel Processors Development Issues in Fuel Cell Vehicle Applications

Richard J. Bellows
Paul J. Berlowitz
Exxon Research & Engineering

PEM FUEL CELLS



***P**roton **E**xchange **M**embrane Fuel Cell*

$H_2 = 2\ H^+ + 2\ e^-$ Anode Cathode $1/2\ O_2 + 2\ H^+ + 2\ e^- = H_2O$

- **Electrochemical Conversion of H_2 to Electric Power**
  - **High power density, low temperature (80-100°C) operation**
  - **No CO, NO_x, HC, PM emissions**
  - **High Efficiency**

- **Vehicle and Stationary Applications**

- **H_2 Fuel Requirement is Major Hurdle**

MAKING HYDROGEN FOR PEM FUEL CELL S

Key Fuel Requirements Of PEM Fuel Cells:
- **Hydrogen-containing gas as fuel**

Fuel Cell Does Not Need Pure H_2 To Operate Efficiently
- **A fuel reformate can contain substantial CO_2, N_2 concentrations**
- **Reformate cannot contain impurities which poison Pt electrode**
  - **e.g., CO, reactive hydrocarbons, oxygenates, ammonia, etc.**

Nearly Any Hydrocarbon Can Be Reformed to Produce H_2 Containing Gas
- **Methane/methanol to coke/coal**
- **Practiced commercially in large industrial plants**
- **H_2 production and management is a key in oil refining**

EVALUATING FUEL OPTIONS

Technology
- Does the PEM vehicle/fuel system meet performance expectations?
  - Vehicles: quick start, fast transient response
  - Stationary: less demanding, possibly nearer to steady-state operation

Economics And Marketing
- Is ownership cost comparable to alternatives?
  - Including purchase price, maintenance, insurance, fuel
  - Safety considerations: e.g., H_2, CO safety in residential installations
- Large, high-risk investments in fuels, vehicles, power sources

Environmental Impact
- How do emissions/efficiency compare on a "resource-to-wheel" basis?
  - Emissions that affect local air quality: CO, NO_x, HC, PM
  - Net CO_2 production, from energy resource to end use

Infrastructure and distribution
- Fuel availability, reliability of supply

HYDROGEN OPTIONS FOR FUEL CELLS

Centralized Production and Retail Distribution of H_2

Production & Storage at Local Site

H_2 produced by steam reforming of variety of fuels (e.g., nat. gas)

Less efficient production in smaller quantities

On-Board Reforming of Alcohols, Hydrocarbons

Technology for vehicle applications

Issues

- Costs and benefits of each option
- Safety, health, environmental impact of production & distribution

VEHICLE H_2 PRODUCTION: FUEL REFORMING

Hydrocarbons, Alcohols are Chemical H_2 Carriers, e.g.,

- $C_8H_{18} + 4\ O_2 + 8\ H_2O = 17\ H_2 + 8\ CO_2$ **(Partial oxidation + Water-Gas Shift)**
- $CH_3OH + H_2O = 3\ H_2 + CO_2$ **(Steam Reforming)**

Liquid Fuel Advantages

- **High energy density**
- **Relatively easy to handle in transport and retail sale**
- **Many hydrocarbons compatible with existing fuel infrastructure**

Challenges

- **High temperature reactions required to convert fuels to $H_2 + CO_2$**
- **Vehicles need new class of chemical reactors**
  - **Compact, efficient, low cost**
  - **Rapid startup, good transient response**
  - **Robust to automotive environment**

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"GASOLINE" FOR VEHICLE HYDROGEN PRODUCTION

Advantage: Widely Available, Inexpensive, Consumer Acceptance, Fuel Flexibility

Liquid Fuels From Petroleum and/or Other Sources (e.g, Ethanol)

- Large potential reserves, distributed worldwide

H_2 From POX/SR followed by Water-Gas Shift

- POX: $C_8H_{18} + 4O_2 = 8\ CO + 9\ H_2$ + Heat
- Steam Reforming: $C_8H_{18} + 8\ H_2O$ + Heat $= 8\ CO + 17\ H_2$
- Water-Gas Shift: $CO + H_2O = CO_2 + H_2$ + Heat
- Autothermal point balances heat input/output of POX/SR

Fuel Processing Consumes up to 20% of Fuel Heat Value

Concerns

- What impurities will cause problem with reformer?
- High temperature needed for soot-free operation
- Heat integration more difficult, system more complex than methanol

US FUEL DISTRIBUTION FACTS

- 180^+ Refineries, 300,000 Tank Cars, 100,000 Tank Trucks
- Gasoline Distribution
  - 110 billion gallons (7 Million BBL/day) sold annually
  - 70,000 miles of pipeline, 800 product terminals, 200K retail stations
- Methanol Distribution
  - Very few retail outlets (<100) -- mostly M-85
  - Transport by tanker truck, tank car
  - Large scale methanol production would be entirely outside continental US
- Natural Gas Distribution
  - Available widely in some regions via pipelines to industrial and residential sites
  - Domestic and direct pipeline imports (Canada)
  - Shipped overseas as LNG
  - Worldwide "excess" capacity is located remotely

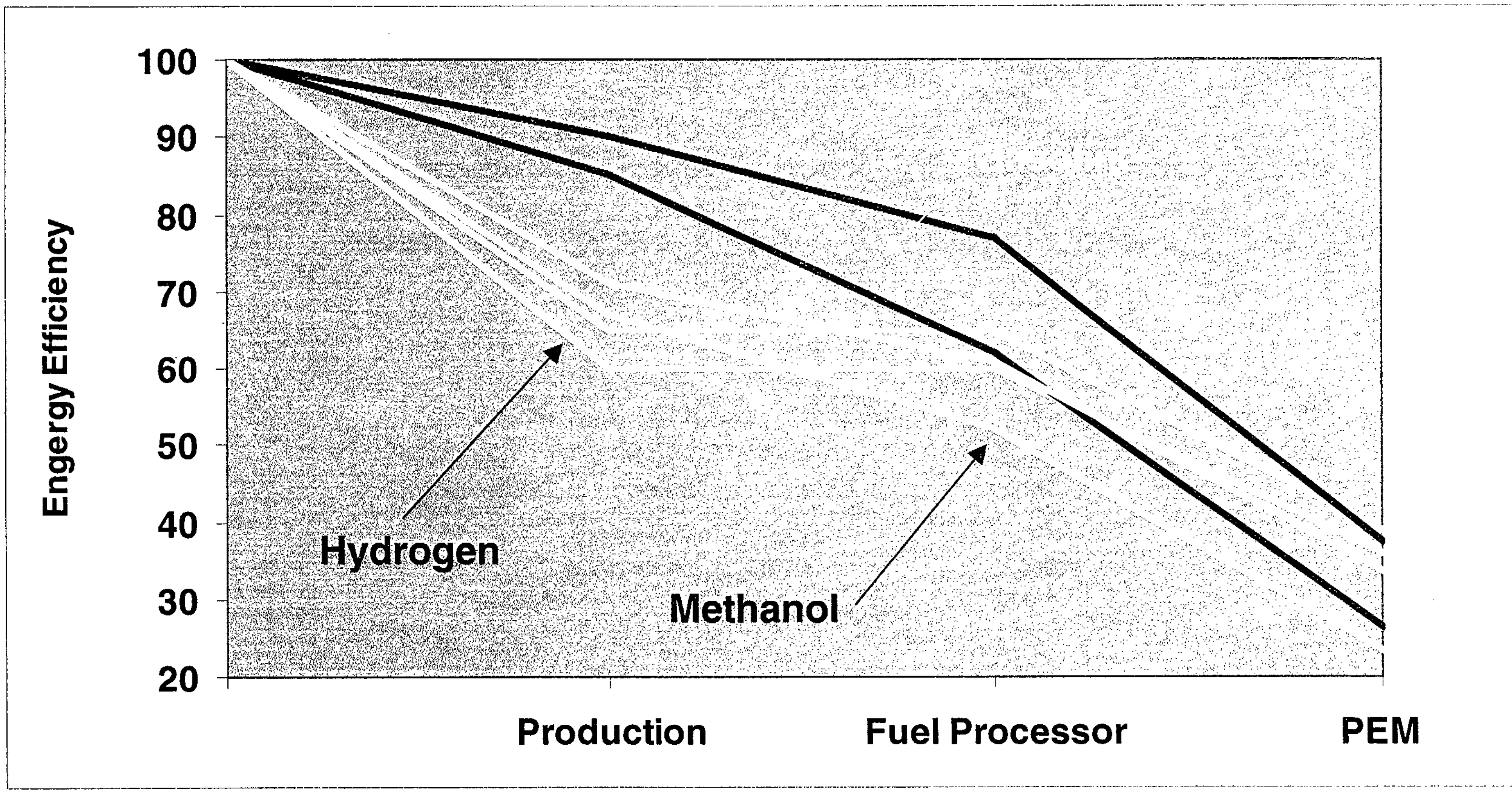
ENERGY EFFICIENCY CONSIDERATIONS

- Many Factors Determine Net Efficiency of Vehicle/Fuel System
  - Consider energy losses in:
    - Resource extraction
    - Conversion of resource to useable fuel (refining, reforming)
    - Distribution (transport, pumping, compression, refueling)
    - Utilization (engine efficiency)

- Energy Efficiency Estimates for Fuel Cell Vehicle Systems
  - Production and distribution best known figures
    - Large scale industrial production practiced for decades
    - Distribution efficiency can vary depending on fuel type, location
  - Fuel Processor not needed for hydrogen
    - Figures for Methanol and Gasoline have large uncertainty
    - Transients, start-up/shut-down, drive cycle all have large impact
  - PEMFC efficiency better understood
    - Improvements in performance possible
    - Efficiency influenced by use, transients, cycle

ENERGY EFFICIENCY ESTIMATES

- **High/low Ranges Shown For Each Fuel**
- **Based on Estimates in Open Literature**



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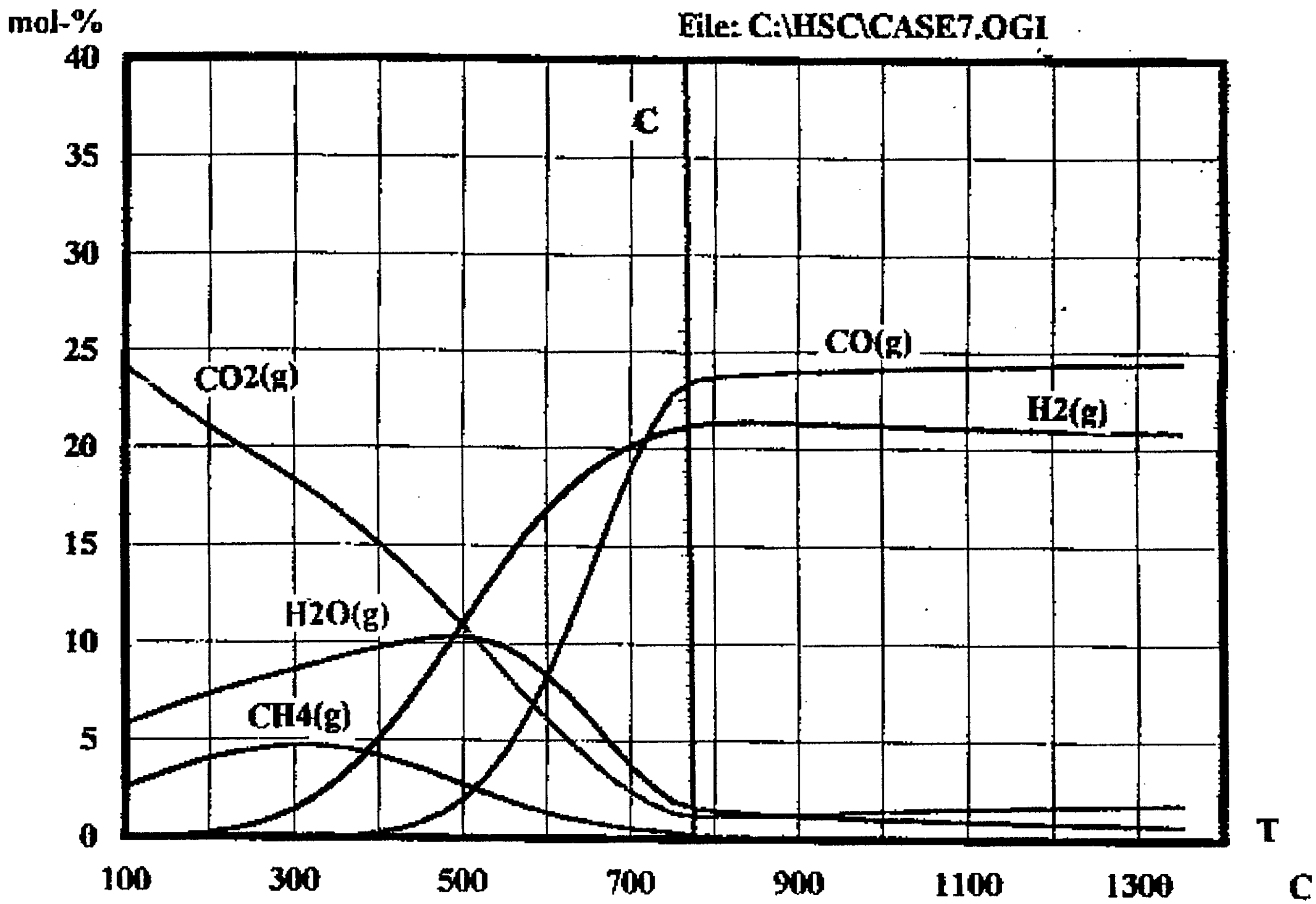
Fuel Train Strategy

→ POX → ($18\% H_2$, $16\% CO$) → WGS → ($33\% H_2$, $1\% CO$) → PROX → ($32\% H_2$, 40 ppm CO) → O_2 Bleed / PEFC

	POX	WGS	PROX	O_2 Bleed / PEFC
Good	Exothermic Rapid Trans. Response Simple- No Cat Catalysts Help	Conv. Poison to Fuel Rapid Initial Kinetics Rapid Trans. Response Commercial Technol.	Init. Select. Good	Restores Pure H_2 Voltage Easy
Bad	CH_4 Slip	CO Slip Final Kinetics Slow	Transient Response Final Select. Poor Temp. Control	Limited to 40 ppm CO H_2 Losses 100X CO
Ugly	Soot	S, Cl- Sensitiv. Sintering at 550 & 260°C	CO & CH_4 Generation	

Reformer Temperature Affects Product Ratios
(Basis: H/C = 1.8, O/C = 1.1, 3 atm.)



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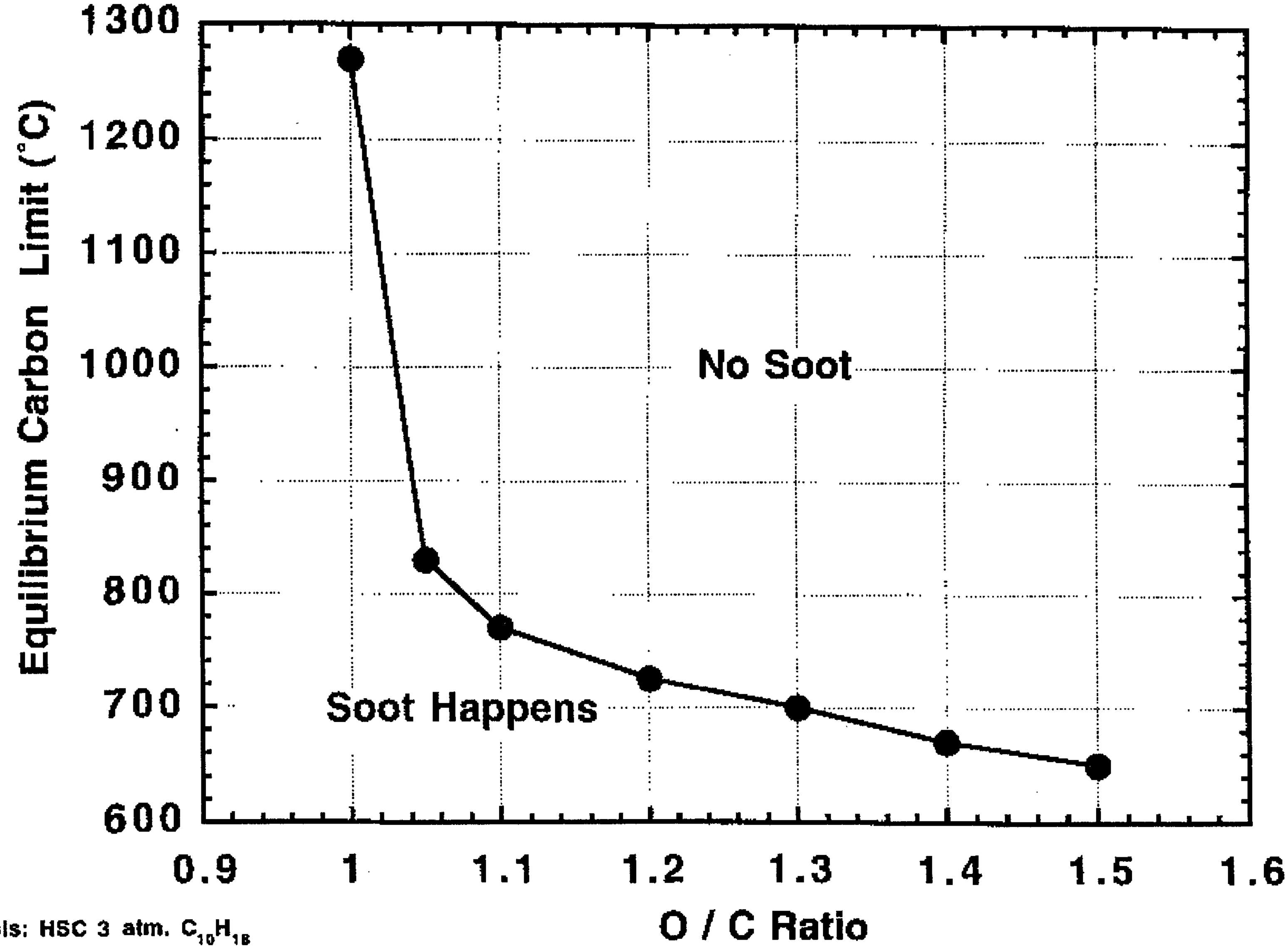
Carbon Deposition Limits - Air POX



Basis: HSC 3 atm. $C_{10}H_{18}$

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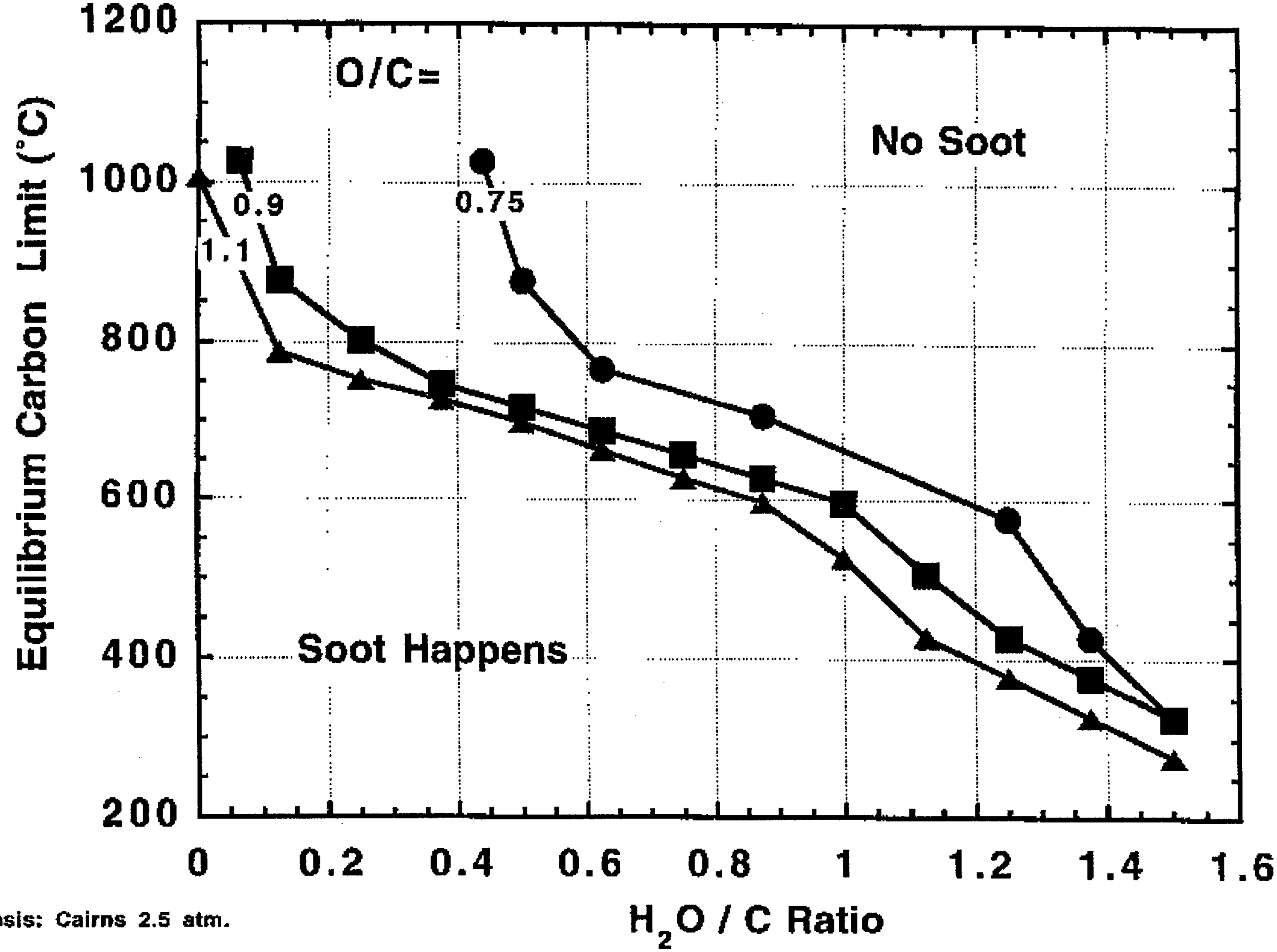
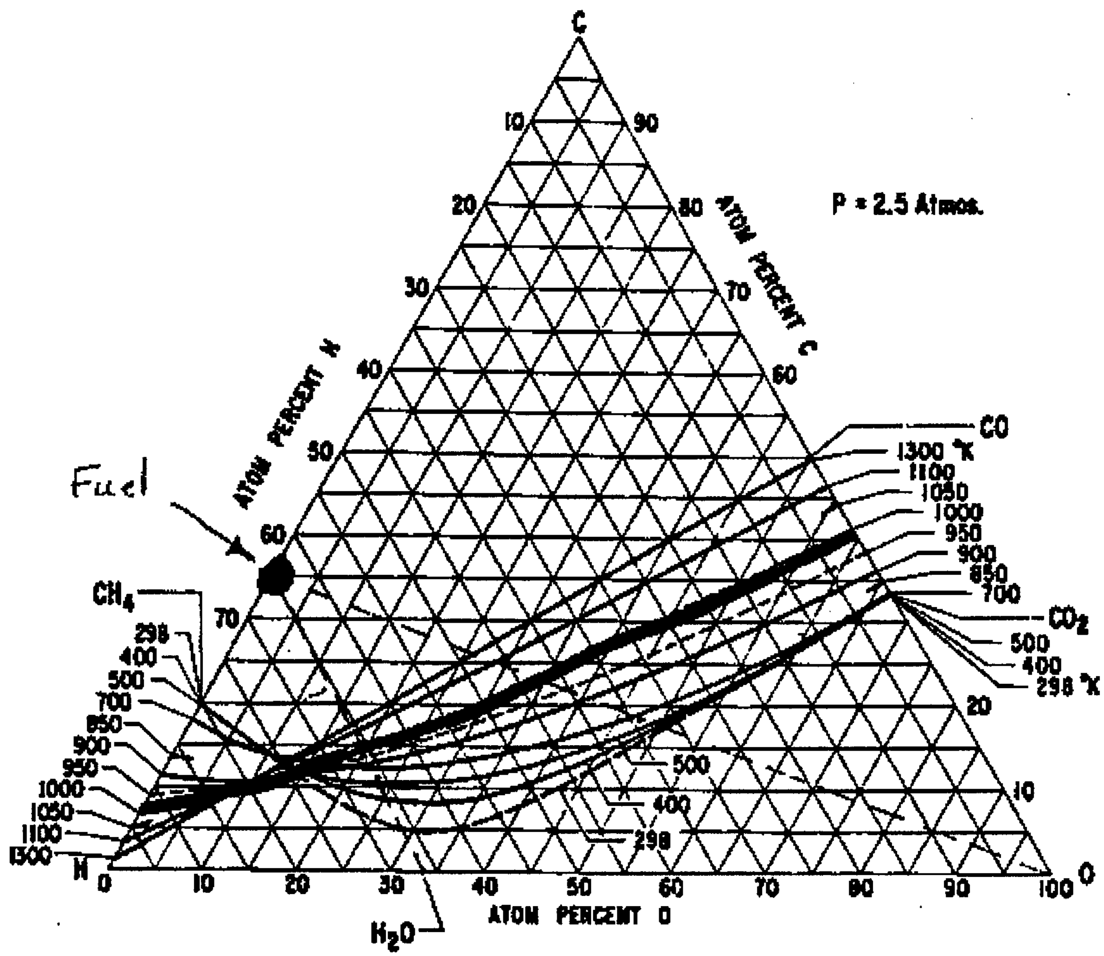
Carbon Deposition Limits vs Water Addition
Feed: O/C = 0.75-1.1 plus extra H_2O / C



Basis: Cairns 2.5 atm.

Carbon Deposition Depends on C/H/O Ratios and Temperature



WATER GAS SHIFT (WGS)

- Base Case - No Alternatives, Good Reaction

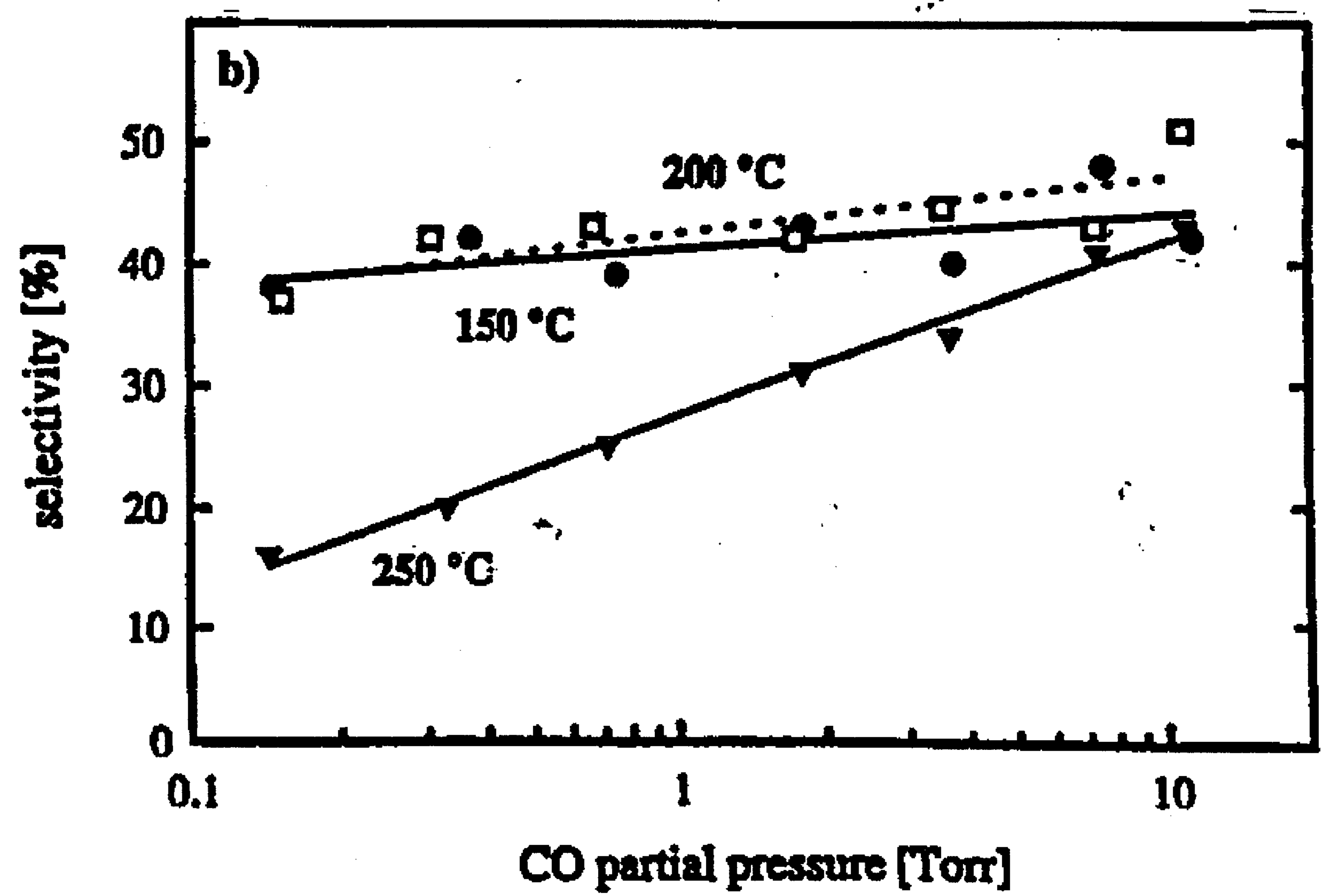
$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

- Well Known Characteristics, Widely Practiced
  - Mildly exothermic
  - Equilibrium limited conversion
    - + HTWGS Fe/Cr oxides, 75% conversion, 550°C max.
    - + LTWGS Cu/ZnO, 94% conversion, 250°C max.

- Issues
  - Volume / weight
  - Start-up time / warm-up transient

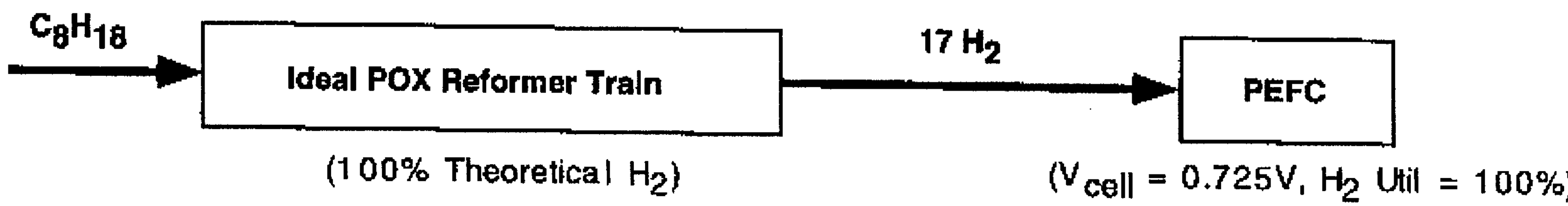
PROX Selectivity Decreases at High Conversion

(J.Cat., 170, 1 (1997))



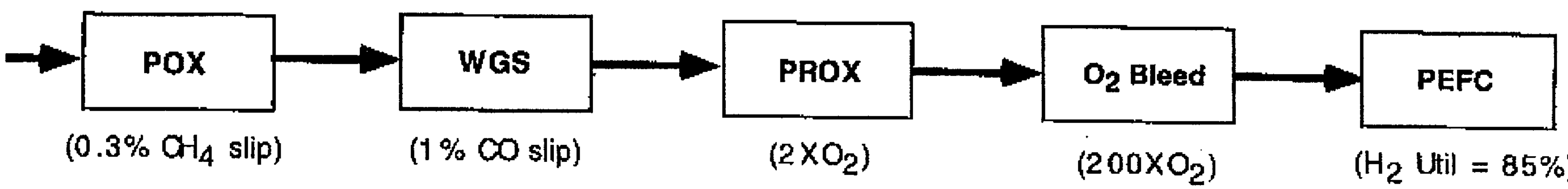
Overall System Efficiency for i-Octane POX Reformer Train

Ideal:



$$\underset{81.2\%}{\eta_{train}} \times \underset{57.9\%}{\eta_{fc}} = \underset{47.0\%}{\eta_{ideal}}$$

Practical:



$$\underset{96.8\%}{\eta_{CH4}} \times \underset{97.3\%}{\eta_{CO}} \times \underset{97.3\%}{\eta_{prox}} \times \underset{97.7\%}{\eta_{bleed}} \times \underset{85\%}{\eta_{H2\ util.}}$$

$$\times \underset{47.0\%}{\eta_{ideal}} = \underset{35.8\%}{\eta_{pract.}}$$

Part II: Hydrocarbon Processor Development Issues

- Operability

- Life

- Cost

- Capabilities
  - Fast Start
  - Transient Response
  - Turndown Ratios

- Optimization
  - Efficiency
  - Weight
  - Volume

- Competing Technologies – Internal Combustion Engine

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Logistic Fuel Processor Issues

- Higher Boiling Range (150-370 vs 40-200°C)
  - Coking possible during vaporization
  - Need short residence times
  - Limit heat exchanger temperature

- Lower H/C Ratios (1.6 vs 1.8)
  - Closer to soot
  - Needs more O than gasoline or CH_4

- Higher Sulfur Levels (500-2000 vs 0-50 ppm)
  - H_2S poisons low temperature shift and anode catalyst
  - Need sulfur traps ($ZnO + H_2S$)
  - Need in line sulfur adsorbents

- Aqueous Impurities (NaCl, carbonates, sulfates)
  - Solids accumulate on heat exchange, catalyst surfaces
  - Cl^- poisons low temperature shift catalyst

Conclusions

- Hydrocarbon Processor Must Compete with Existing Technologies
  - Operability
  - Life
  - Cost
- Logistic Fuels more Difficult to Process than Gasoline
  - Higher boiling range
  - Lower H/C
  - More S
  - Aqueous impurities

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Fuel Processing using Microsystems

Anna Lee Y. Tonkovich
Battelle, Pacific Northwest Division

June 17, 1999

Pacific Northwest National Laboratory

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  - DOE - EE Office of Transportation Technology
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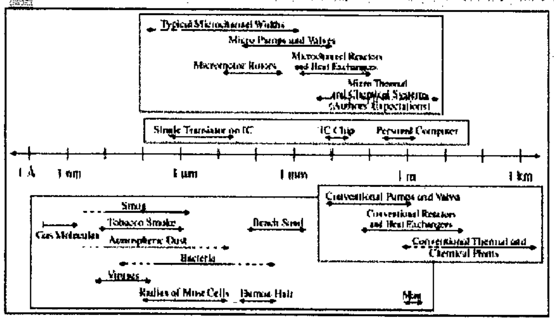
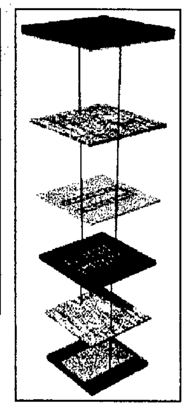
  - Bob Wegeng - Microsystems Initiative Leader
  - Eric Daymo - Portable Power Technology Leader
  - Michele Friedrich - Heat pump task leader
- **Team at the Northwest Division**

Pacific Northwest National Laboratory

Microsystems:
A New Class of Process Technology





Exploitation of Heat and Mass Transport Advantages in Engineered Microstructures

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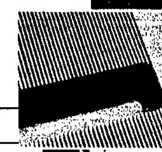
Technology Comparisons

- **Microsystems**
  - Parallel processing -- dominated by wall effects
  - Economy of mass production
  - Compact hardware with high throughput
  - Economically viable at high or low throughput



- **Conventional process hardware**
  - Bulk processing – dominated by bulk flow
  - Economy of scale
  - Large hardware with high throughput
  - Economically viable only at high throughput

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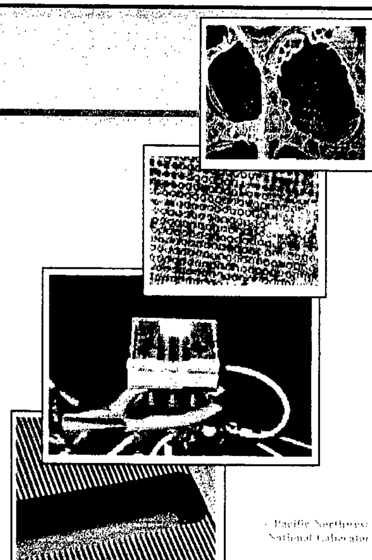
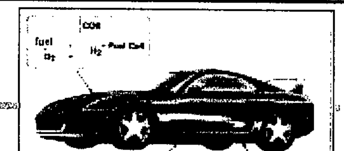
Microsystems

- **Components**
  - Reactors
  - Separators
  - Heat exchangers
  - Combustors
- **Systems**
  - Fuel processor
  - Heat pump



Microsystems

- **Applications**
  - Automotive power
  - Portable power
  - Cooling
  - Space exploration
  - Environmental remediation
  - Carbon management



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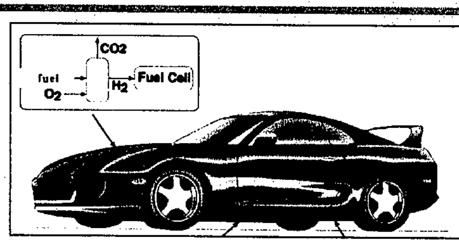
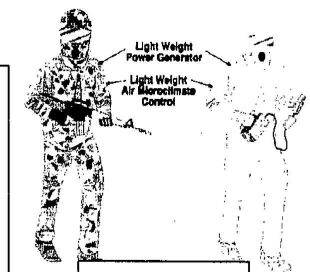
Application:
Automotive Power

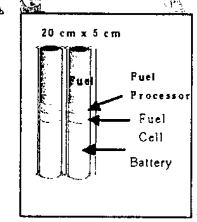


- **Efficiency**: 50% vs. 20% for IC engine
- **Issues**: Size and cost
- **Impact**: 58% reduction in CO_2 per mile traveled

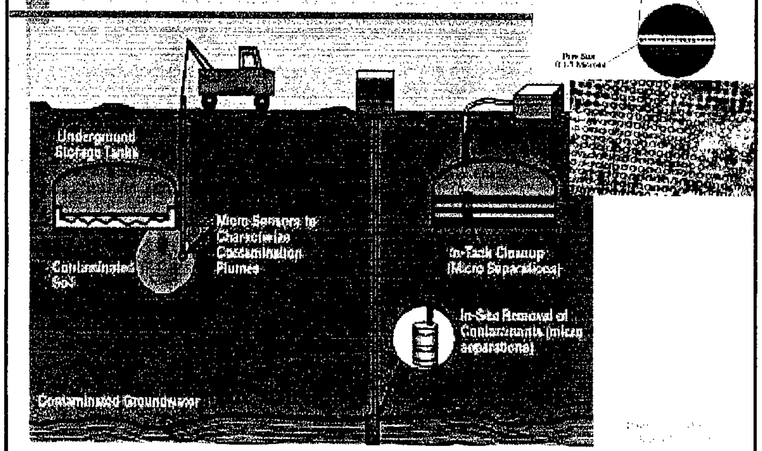
Application:
Portable Power

- **Goal**
  - Long duration continuous power
  - Low weight and volume
- **Technology Need**
  - Compact H_2 generation
  - Compact fuel cell
- **Energy content**
  - Diesel: 13.2 kW-hr/kg
  - H_2 storage: 0.5 kW-hr/kg (metal hydrides)
  - Batteries: 0.110 kW-hr/kg





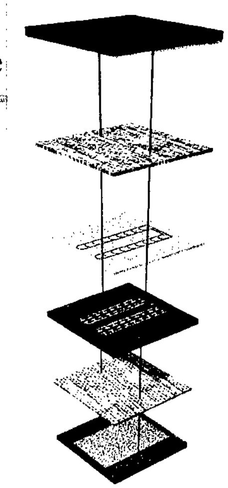
Application:
Environmental Remediation



Microsystems:
Process Development at Battelle

Laminate Sheet Architecture

- Multiple microcomponents per sheet enables scale-up
- Each sheet performs one or more unit operations
- U.S. # 5,611,214 (issued 3/18/97)
- U.S.# 5,811,062 (issued 6/11/98)
- Others pending (U.S. and foreign)



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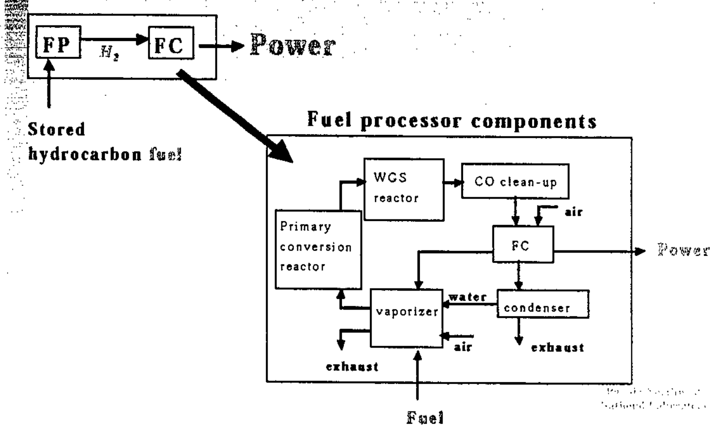
Microsystems:
Low Cost Fabrication at Battelle

Economy of mass production, <u>not</u> economy of scale

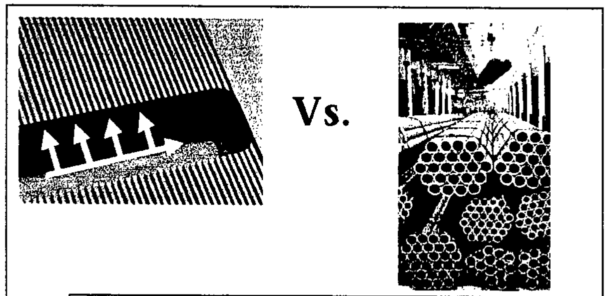
Battelle:
Leading the way in compact process development

- Demonstrating compact microsystems
- Developing new applications
- Building a portfolio of intellectual property
  - Enabling sheet architecture
  - Catalysts
  - Components & systems
  - Low cost manufacturing methods

Fuel Processor System:
Microsystems Enable Compact Power



Why Microsystems?
Enhanced Heat Transfer



- Reduce transport distance
- High surface area to volume ratio
- Low pressure drop through channels

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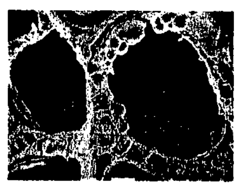
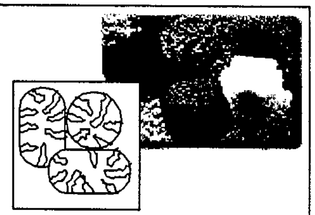
Why Microchannel Reactors?
Enhanced Mass Transfer



Vs.



- Reduce transport distance
- High effectiveness factor

Automotive Fuel Processor

- Primary Conversion
- Water gas shift
- CO Clean-up
- Vaporizer

Primary conversion:

Automotive System - *Conventional* Hardware

	Partial Oxidation	Autothermal Reforming	Steam Reforming
Pros	• Fast kinetics • Compact process • Fast transient response • Fewer components	• Balanced heat duty • Simplified flowsheet	• No air compressor • High H_2 in reformate
Cons	• Air compressor • N_2 dilution • High temperature • $$ Materials • Safety	• Air compressor • N_2 dilution • High temperature • $$ Materials • Safety	• Large hardware • Slow transient response • High temperature • Thermal integration

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Primary conversion:

Automotive Scale - *Microsystems*

Severely heat transfer limited

	Partial Oxidation	Autothermal Reforming	Steam Reforming
Pros	• Fast kinetics • Compact process • Transient response • Fewer components	• Balanced heat duty • Simplified flowsheet	• No air compressor • High H_2 in reformate • Small hardware • System efficiency ~ 45% • Low system $ • Fast transient response • Modest temperature • Modular for high turndown ratio
Cons	• Air compressor • N_2 dilution • High temperature • $$ Materials • Safety	• Air compressor • N_2 dilution • High temperature • $$ Materials • Safety	• More components required for high efficiency

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Process Chemistry:
Automotive Fuel Processor

- Iso-octane steam reforming (gasoline simulant)
  - $C_8H_{18} + 8\,H_2O = 8\,CO + 17H_2$ $\Delta H_r = 1345$ kJ/mol
  - $CO + H_2O = CO_2 + H_2$ (some high T shift)
  - $CO + CO = CO_2 + C(s)$
  - Cracking reactions
  - Methane formation
  - <u>Conditions (conventional hardware)</u>:
    - Temperature ~ 800C
    - Steam : Carbon ~ 6+
    - Residence time > 1 sec

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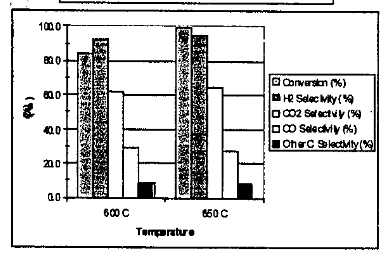
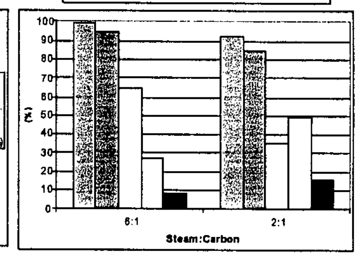
Primary Conversion:
Proprietary Catalyst for Iso-octane Reforming

Temperature effect (6:1 S:C)



Steam ratio effect (650 C)



>90% conversion and >90% selectivity to H_2
at
650 C and 2.3 ms residence time

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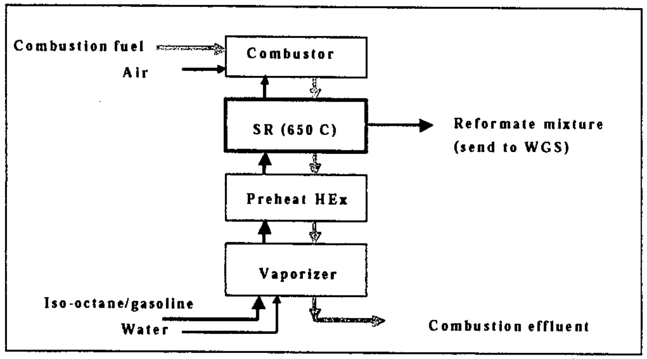
Primary conversion:
Proprietary Catalyst and Microreactor

- Steam reforming demonstrated in a microchannel reactor



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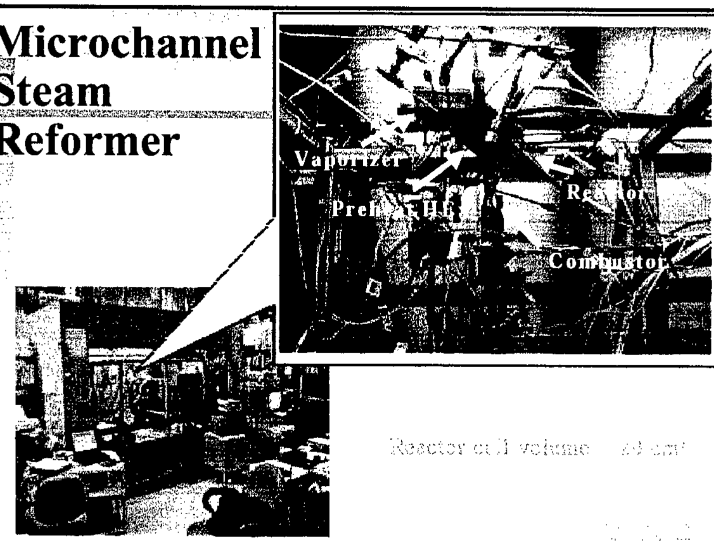
Microchannel Steam Reformer



Reactor cell volume

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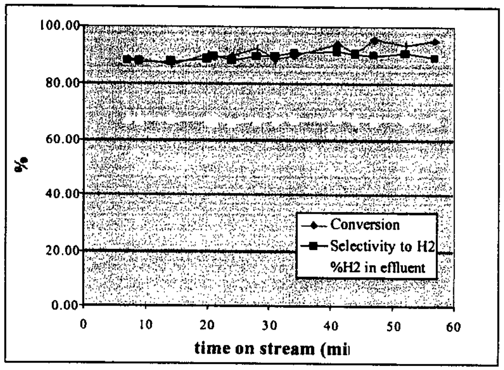
Iso-octane Steam Reforming



τ=2.3 ms
T=650 C
S:C = 6
0.5-kW$_e$

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Steam Reformer Summary

- Demonstrated steam reforming a microchannel reactor
- Capacity (cell volume 29 cm^3)
  - Initial experiments: 0.5-kW$_e$ at 1 atm
  - Design point: 5-kW$_e$ at 5 atm
- Performance
  - Conversion = 93%
  - H_2 Selectivity =91%
  - H_2 content = 67%
  - No degradation observed
- Conditions
  - Residence time: 2.3 milliseconds
  - Steam:carbon : 6:1
- Implications: complete full-scale SR System (50-kW$_e$) ~4L

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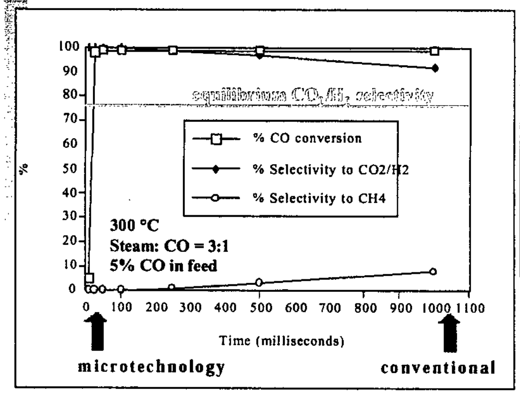
Automotive Fuel Processor

- Steam reformer
- Water gas shift
  - $CO + H_2O = CO_2 + H_2$
  - Methane formation
- CO Clean-up
- Vaporizer

Water Gas Shift reaction:

Fast Kinetics = Compact Process



Non-equilibrium products at short contact times:

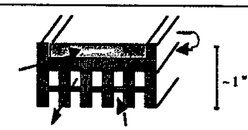
< 80% selectivity to H_2 at equilibrium

>99.9% selectivity observed at 25 ms

Automotive Fuel Processor

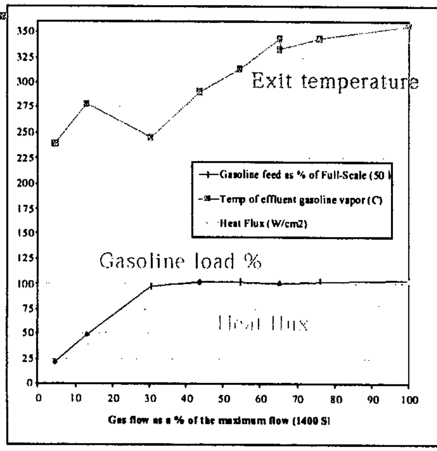
- Steam reformer
- Water gas shift
- CO Clean-up
- Vaporizer
  - Combust dilute H_2 present in anode effluent to provide heat of vaporization for fuel

Full-Scale Microchannel Gasoline Vaporizer



- Attributes: Four parallel cells of microchannel reactors and four cells of microchannel heat exchangers
- Size: 3" by 4" by 1.5"
- Capacity: Vaporized gasoline for 50-kW_e fuel processing system
- Implications: Complete fuel processor system = 0.3 ft^3
- Fabrication: Laminate process
- Pressure drop: $\Delta P < 2$psi through microchannels at 1400 SLPM
- Delivered : Epyx and H2 Burner

Compact Gasoline Vaporizer:
Full-Scale Performance

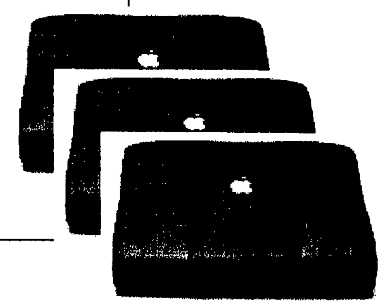


Gasoline vaporized:
~ 300 mL/min

Feed gas (anode effluent + air:
~ 1400 SLPM

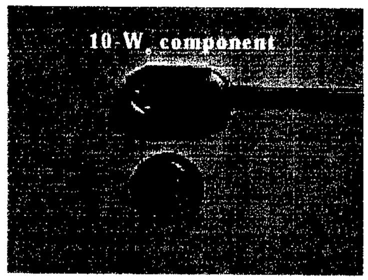
Implications:
50-kW$_e$ Automotive Fuel Processor

- **Components**
  - Vaporizer
  - Primary Conversion
  - WGS
  - CO Cleanup
- **System Volume**
  - Total ~ 8 L
  - *Less than 3 laptops*



Implications:
Portable Power

- **Components (includes reactor and HEx)**
  - SR
  - WGS
  - PrOx
- **System Volume**
  - < 2 cm x 2 cm x 2 cm



Research Challenges and Needs

- Microfluidics and heat transfer
- Surface effects/forces
- Fouling, reliability, maintainability
- Lifetime
- Actuators, control elements, and control systems
- Ultimate manufacturing costs

Conclusions

- Microchannel reactors enable miniaturization of fuel processing components
- 50-kW_e automotive fuel processor ~ 8-L in total volume
- 10-W_e portable fuel processor < 8-mL in volume

Partial Oxidation in Millisecond Reactors

Lanny Schmidt
University of Minnesota

Monolith Reactors:

- 10,000 microreactors in parallel
- 10 tons/day from a 1 liter reactor

1. Methane to Syngas
2. Ethane to Ethylene
3. Alkanes to Oxygenates
4. Catalytic Wall Heat Exchange Reactor

CATALYTIC PARTIAL OXIDATION OF ALKANES AT MILLISECOND CONTACT TIMES

Lanny D. Schmidt
Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis MN 55455

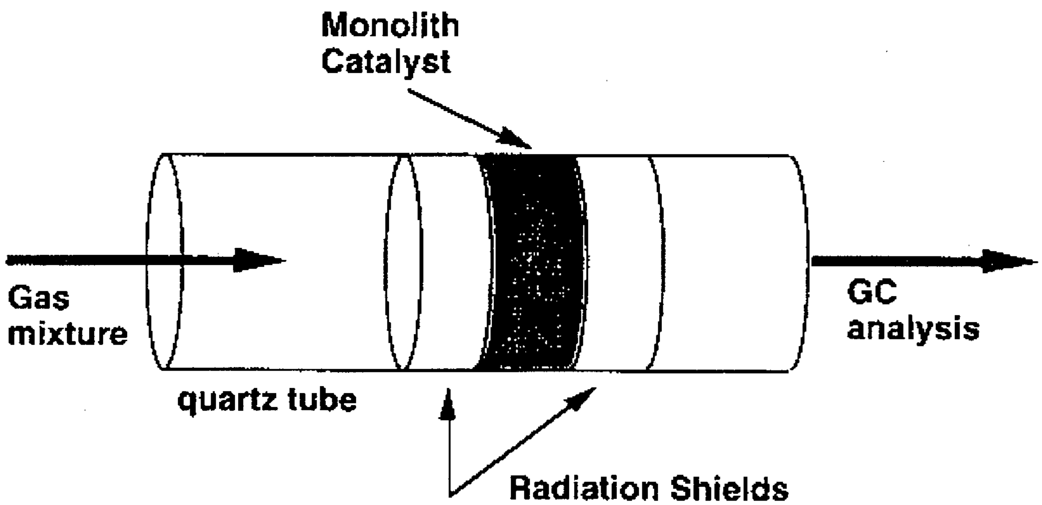
Convert light alkanes to fuels and chemicals
more gas and gas liquids than crude oil
the major technology goal for the next 20 years

Potentially revolutionary
reactor 10^3 smaller
no process heat

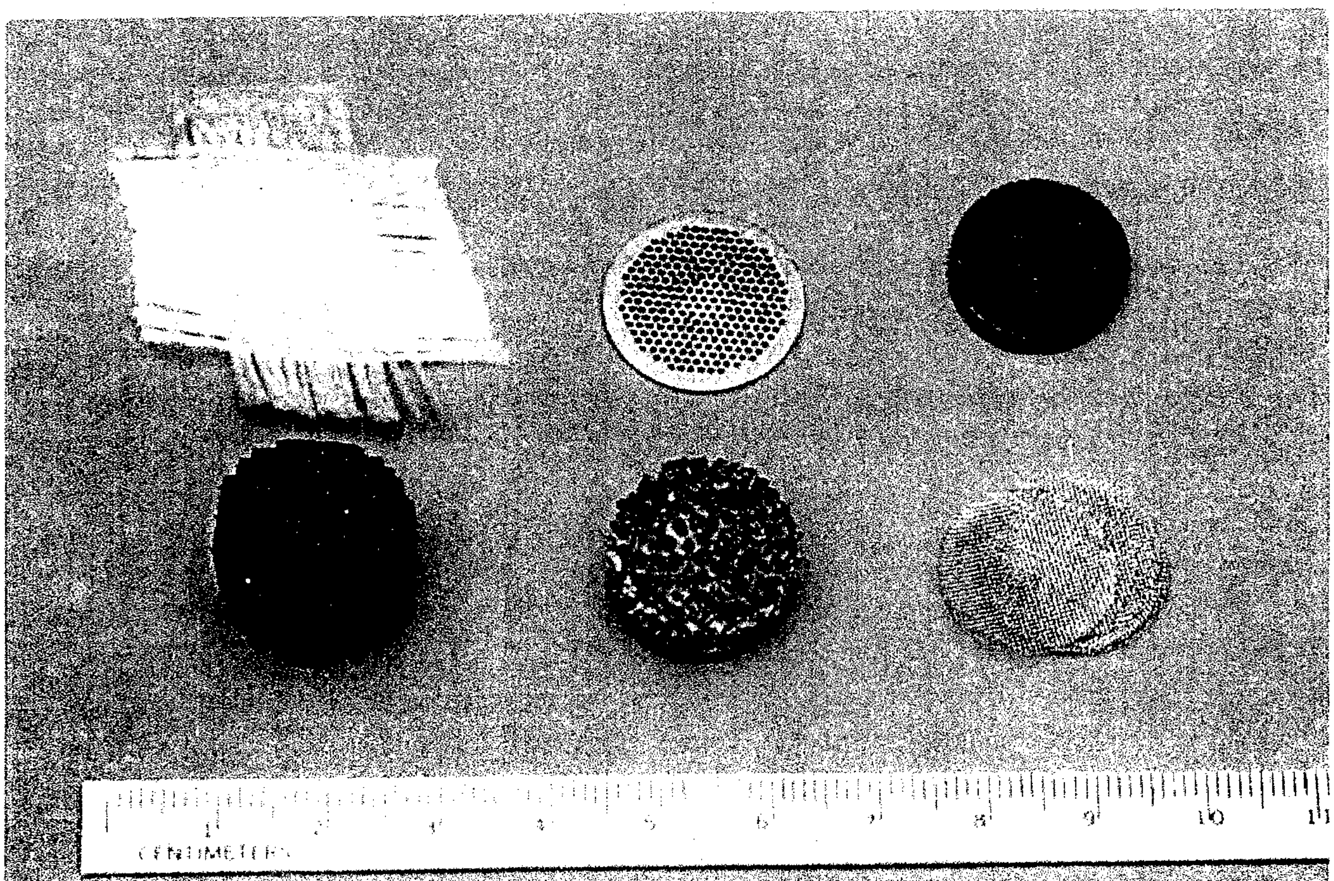
Goes back to 19th Century
Michael Faraday
Ostwald HNO_3
Andrussow HCN

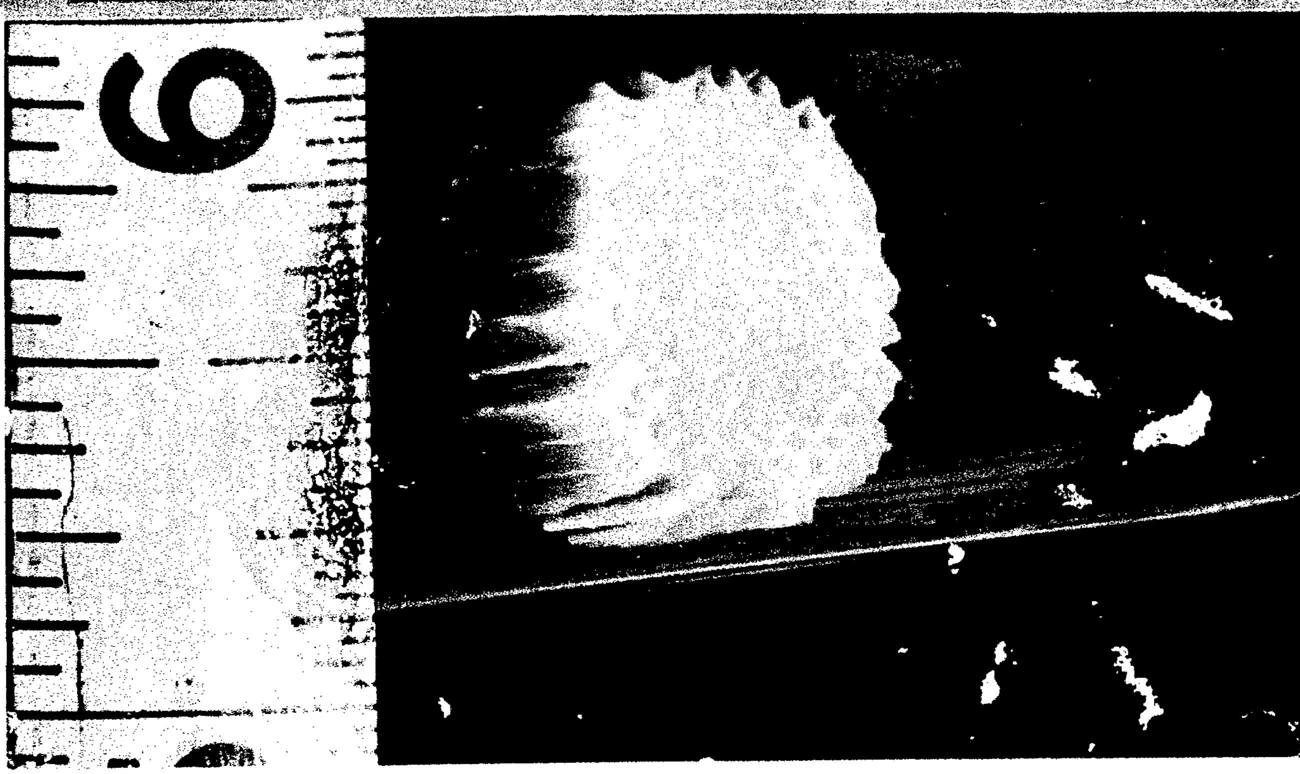
Potentially hazardous

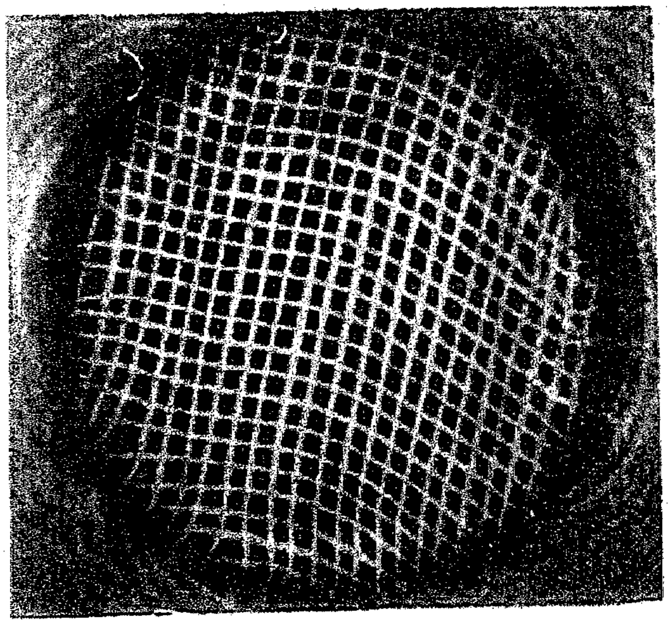
Monolith reactor

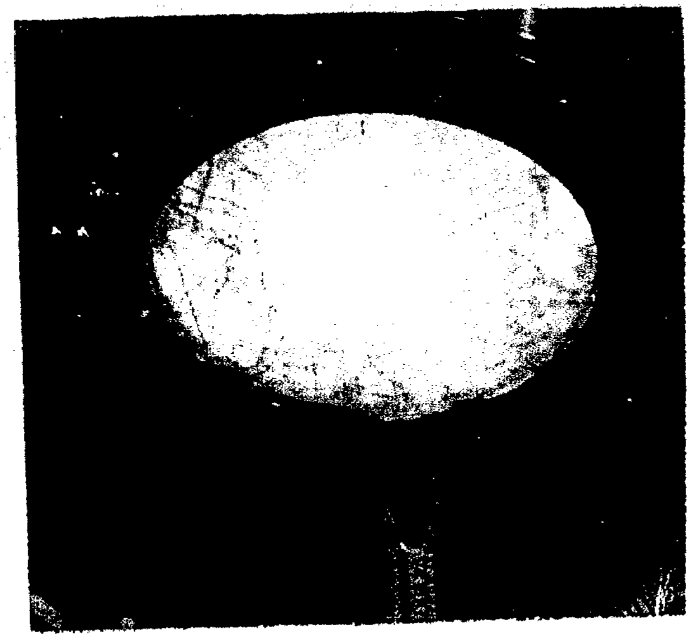


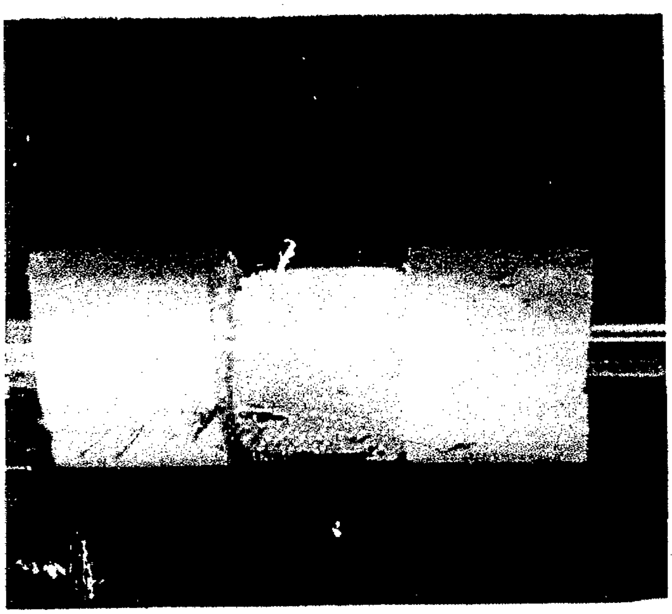
Monolith Catalysts

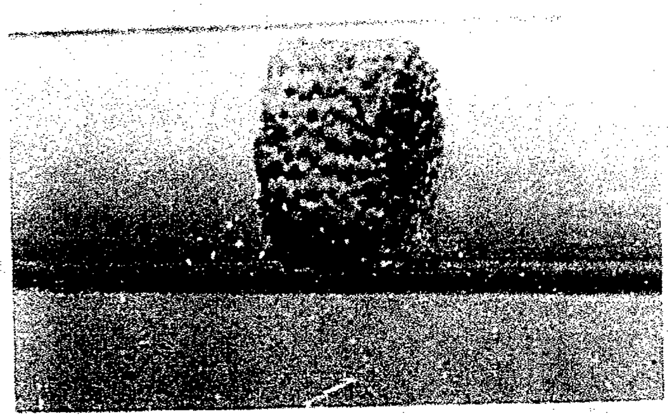


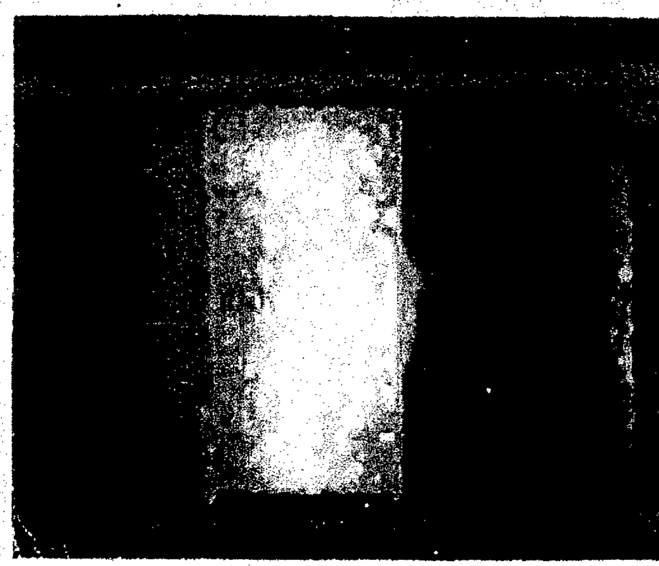












Millisecond Reaction Systems

process	S	X	catalyst
methane to syngas	95%	95%	Rh monolith
methane to HCN	70	90	Pt gauze pack
ethane to ethylene	70	90	Pt monolith
alkanes to olefins	70	90	Pt monolith
butane			
to oxygenates	40	25	single gauze
to olefins	35		
methane to acetylene	25	80	Pt monolith

adiabatic reactor
no preheat
no diluent
$\tau<5$ milliseconds
O_2 conversion is 100%

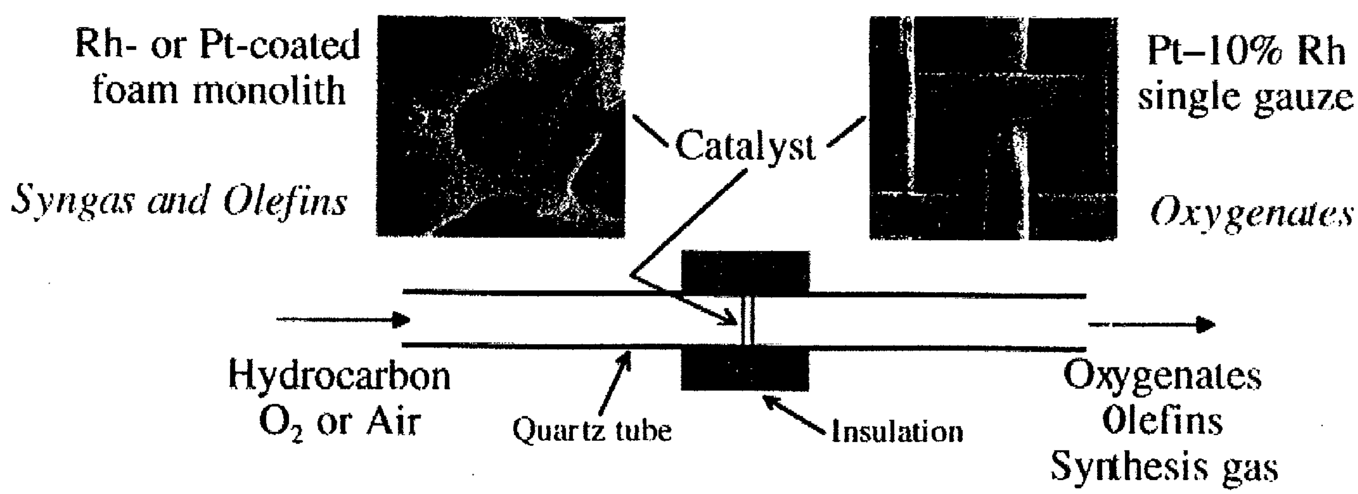
Introduction

➢ Catalytic partial-oxidation reactions can convert alkanes and O_2 or air into useful chemicals with high selectivities:

★ Extremely fast (millisecond time scales)
★ Exothermic, adiabatic, and autothermal operation

➢ Potential to replace industrial processes such as:

★ Steam reforming of methane to make synthesis gas ($CO + H_2$)
★ Liquid-phase partial oxidation to oxygenated hydrocarbons



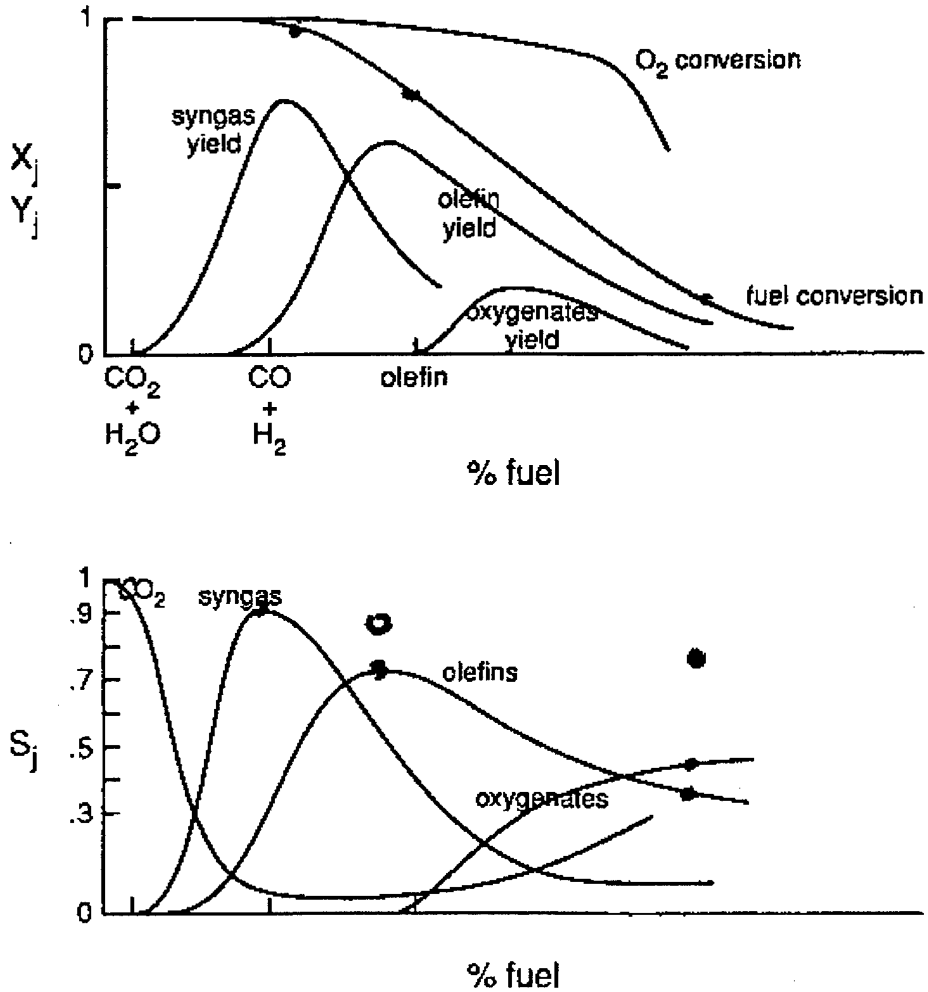

1
0
X_j
Y_j
O_2 conversion
syngas yield
olefin yield
fuel conversion
oxygenates yield
CO_2 + H_2O
CO + H_2
olefin
% fuel
1
.9
.7
.5
.3
0
S_j
CO_2
syngas
olefins
oxygenates
% fuel

Fig. ?

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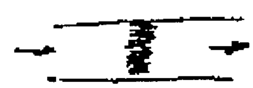
METHANE OXIDATION

$$CH_4 + \tfrac{1}{2}\, O_2 \rightarrow CO + 2H_2$$

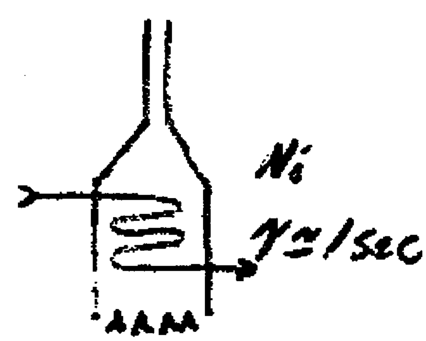
$$+\ 2O_2 \rightarrow CO_2 + 2H_2O$$

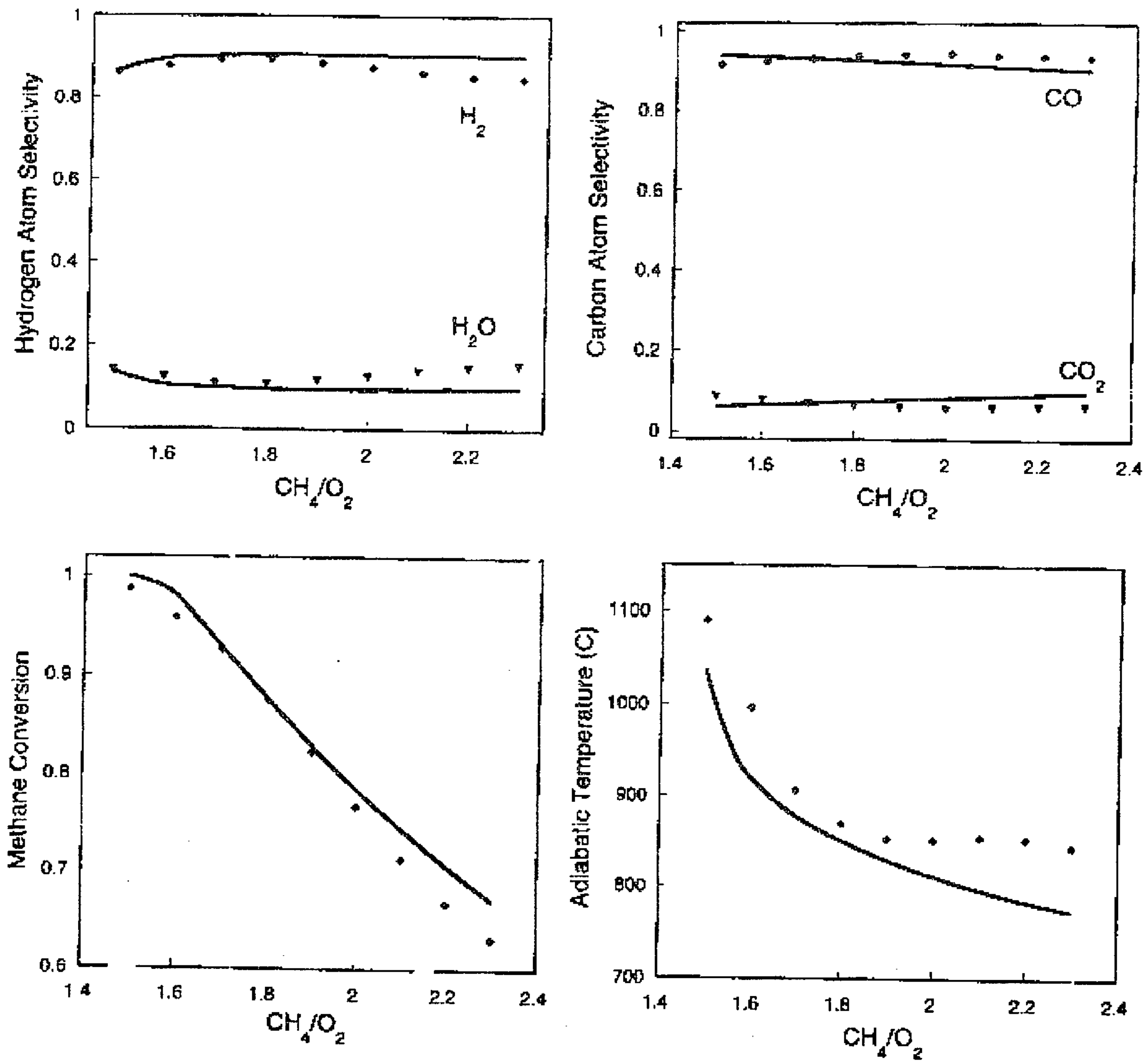
$$\rightarrow C_S + 2H_2$$



steam reforming

$$CH_4 + H_2O \rightarrow CO + 3H_2$$





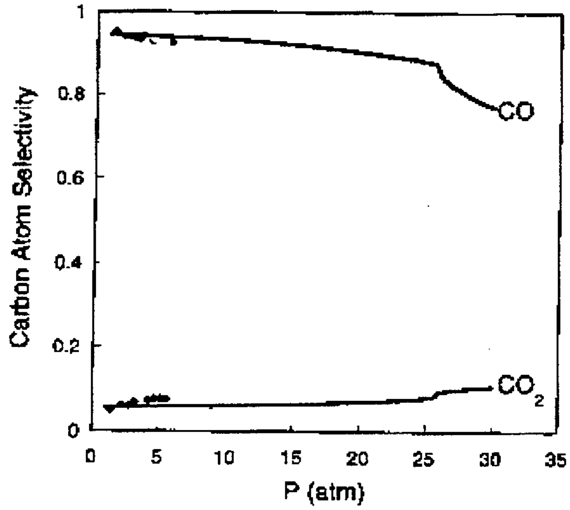
45-ppi Rh monolith catalyst

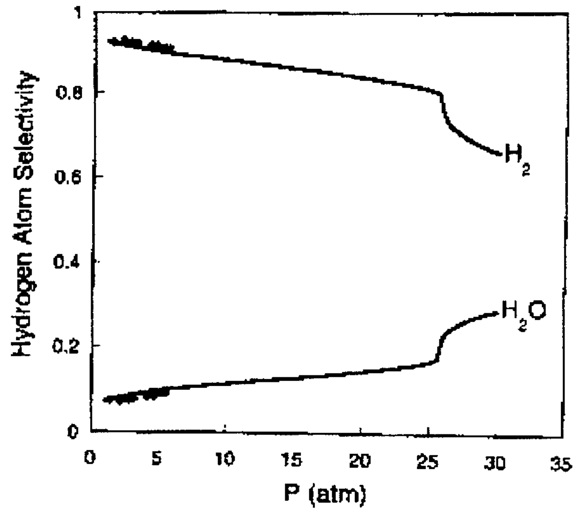
30% N_2 dilution

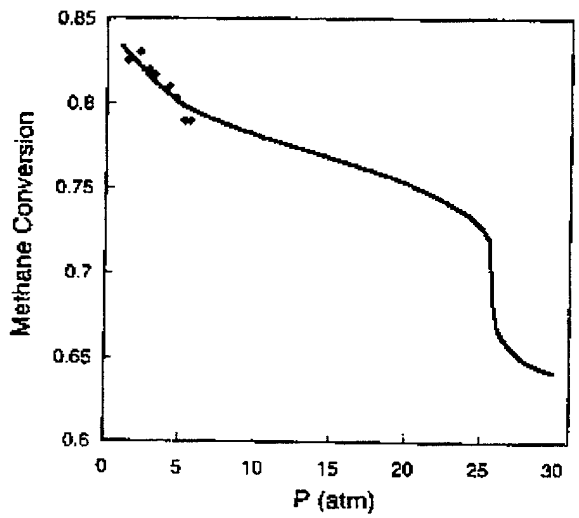
$T_0 = 25$ C

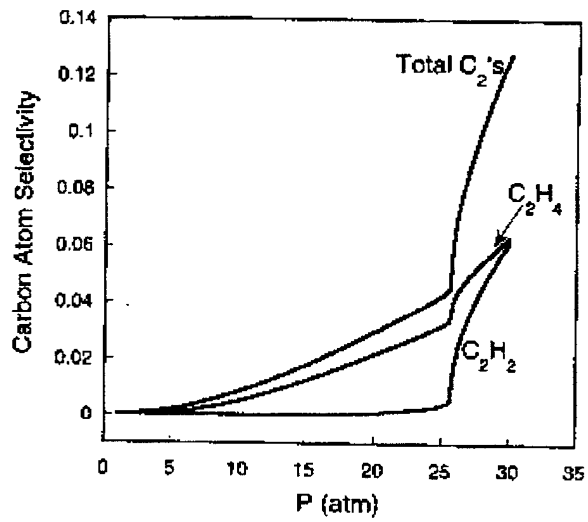
5-ms residence time

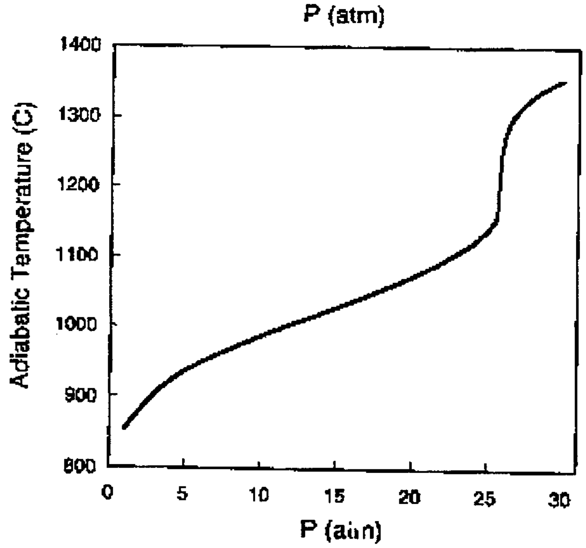
Symbols represent data of Bodke (1997)





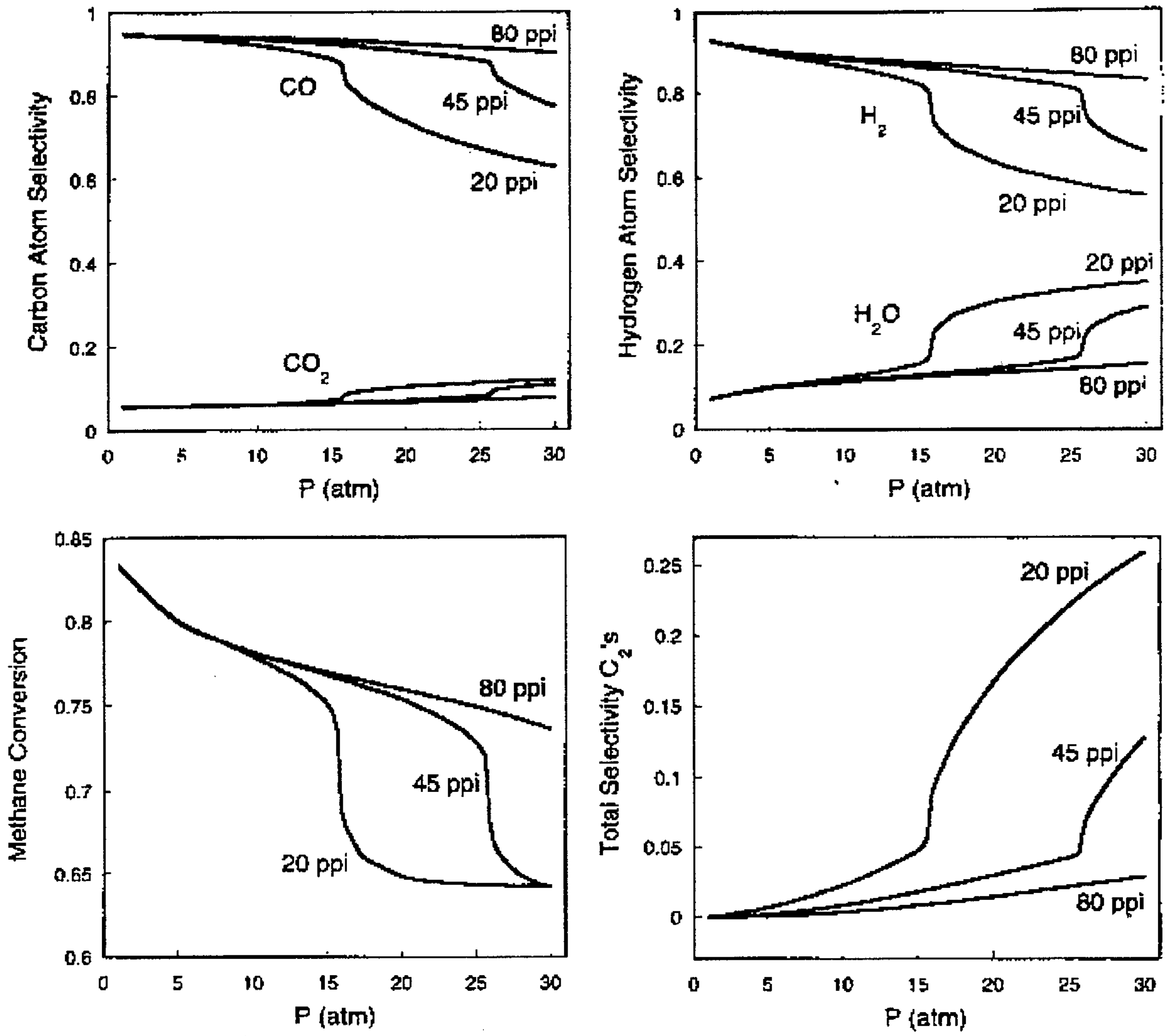


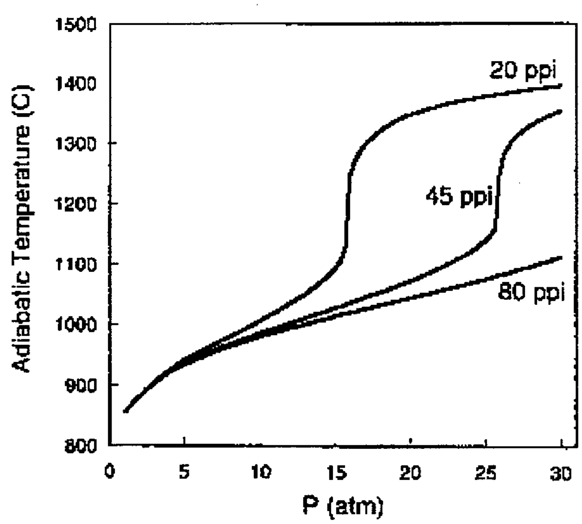




45-ppi Rh monolith catalyst
$CH_4/O_2 = 2.0$
$T_0 = 25$ C
Oxygen
5-ms residence time

Symbols represent
data of Dietz (1995)





Rh monolith catalyst
$CH_4/O_2 = 2.0$
$T_0 = 25$ C
Oxygen
5-ms residence time

SCALEUP

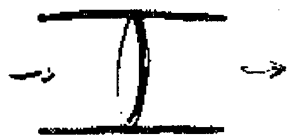
10 l/min, v=1 m/sec, d=1.7 cm, l=1 cm

30 lb/day

of syngas with 5% impurities
or
ethylene with 40% impurities

---

1 foot diameter disc at lab conditions



1.5 tons/day

---

1 foot diameter disc at 30 atm and 10 m/sec
(not proven)

500 tons/day

500 watts → 2MW

1 gram catalyst → 250 grams
100 cm^2 surface area

No deactivation

No coke

ETHANE OXIDATION

$$C_2H_6 + O_2 \rightarrow 2CO + 3H_2$$

$$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$$

$$+ \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

$$\rightarrow 2C_S + 3H_2$$

---

steam cracking

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Mechanism

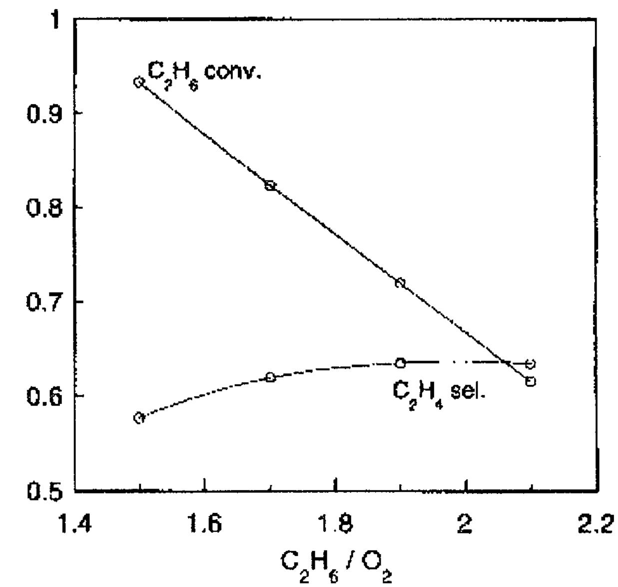
University of Minnesota

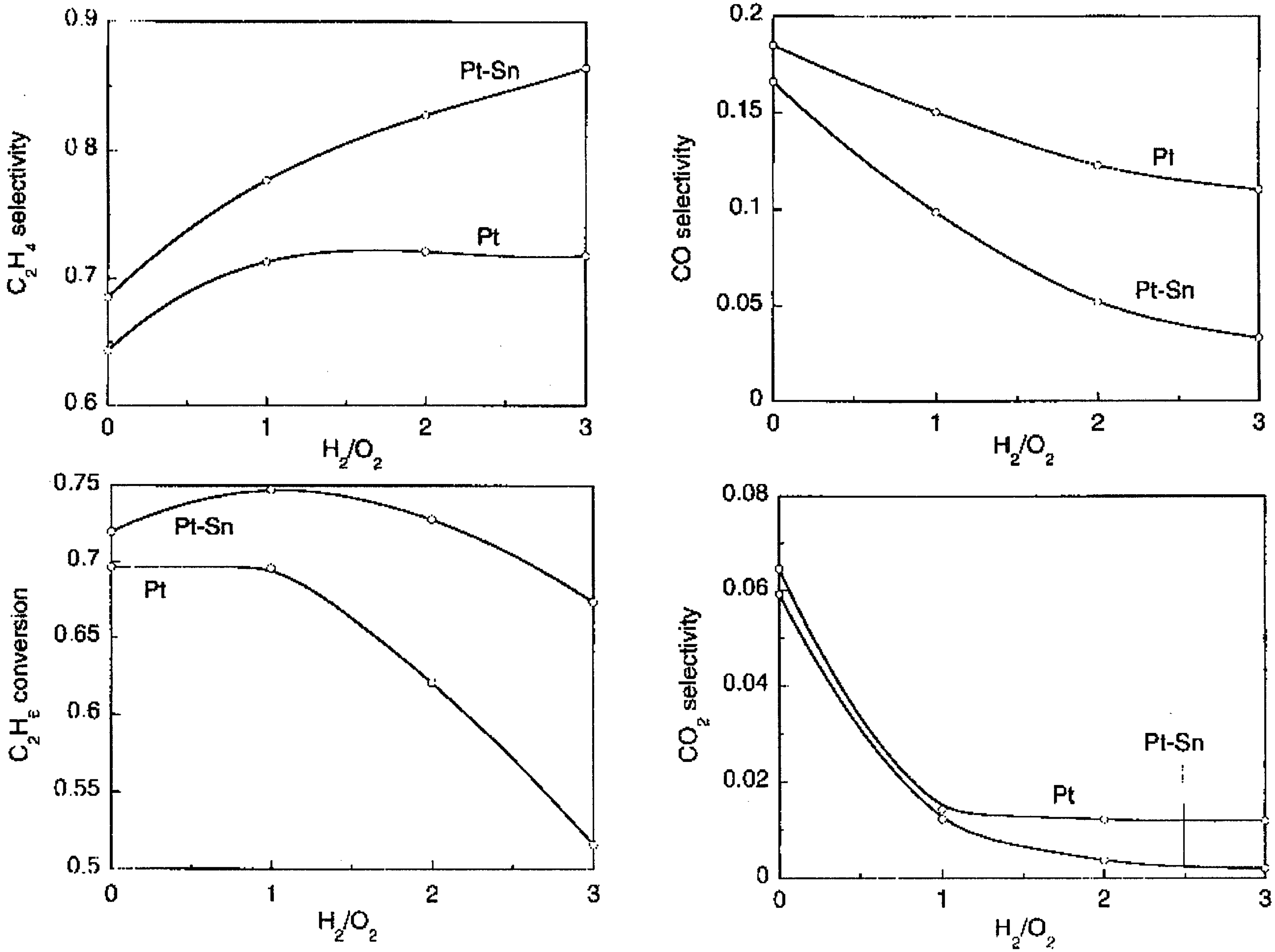
- Coupled exothermic and endothermic reactions
  - $C_2H_6 + O_2 \longrightarrow CO + CO_2$ (35%)
  - $C_2H_6 \longrightarrow C_2H_4 + H_2$ (65%)
- $H_2 + O_2 \longrightarrow H_2O$ instead of $C_2H_6 + O_2 \longrightarrow CO + CO_2$ should improve selectivity to ethylene
- Hydrogen is a major product, easy to recycle
- Will form an explosive mixture with oxygen, careful design of experiments

Partial Oxidation of Ethane to Ethylene

UNIVERSITY OF MINNESOTA

- $C_2H_6 + {}^1/_2\, O_2 \rightarrow C_2H_4 + H_2O$
- Pt/Al_2O_3 catalyst
- 65% C_2H_4 selectivity
- 60% C_2H_6 conversion
- Advantages
  - Residence time ~ 1 msec
  - Exothermic reaction
  - No carbon build-up
  - Negligible emissions




C_2H_4 selectivity
0.9
0.8
0.7
0.6
0
1
2
3
H_2/O_2
Pt-Sn
Pt
CO selectivity
0.2
0.15
0.1
0.05
0
0
1
2
3
H_2/O_2
Pt
Pt-Sn
C_2H_6 conversion
0.75
0.7
0.65
0.6
0.55
0.5
0
1
2
3
H_2/O_2
Pt-Sn
Pt
CO_2 selectivity
0.08
0.06
0.04
0.02
0
0
1
2
3
H_2/O_2
Pt
Pt-Sn

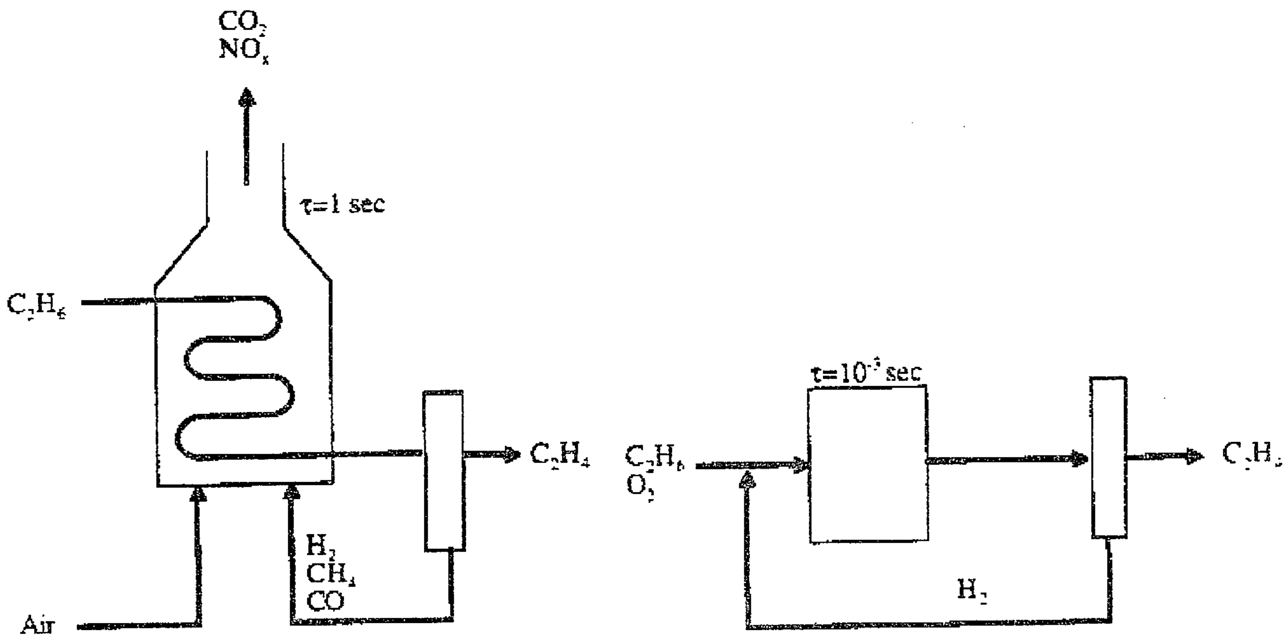
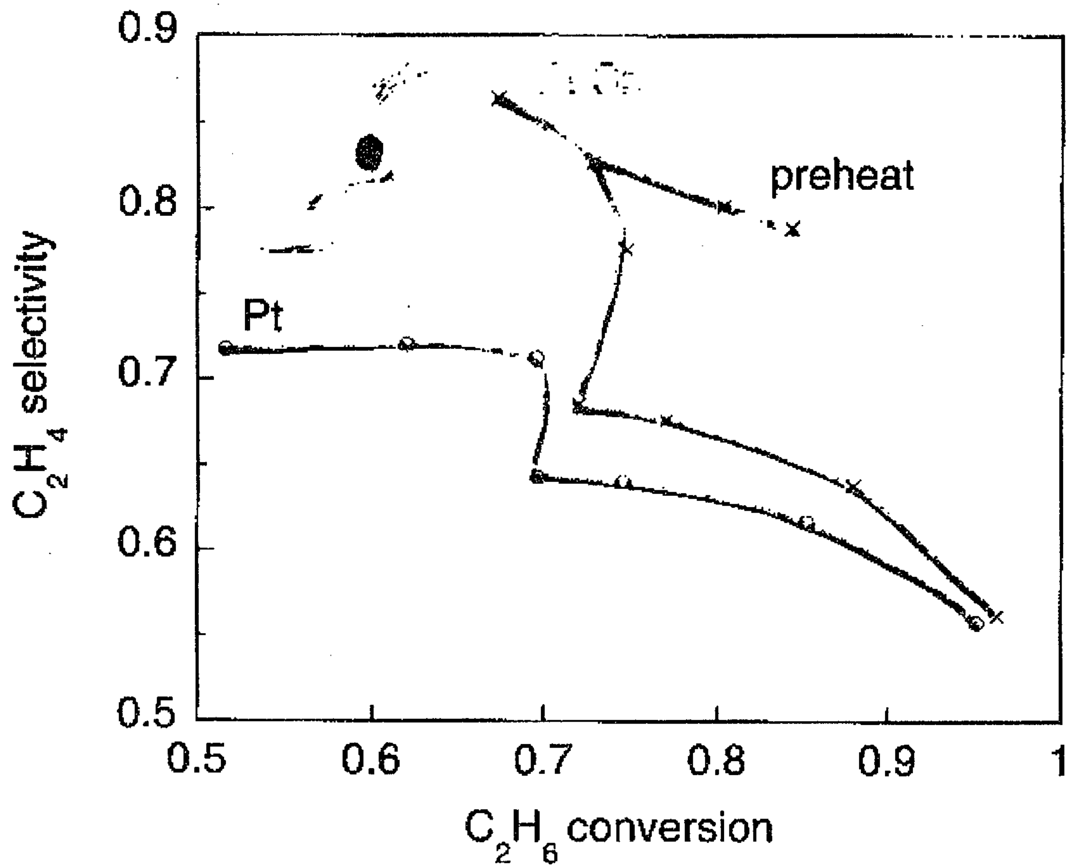


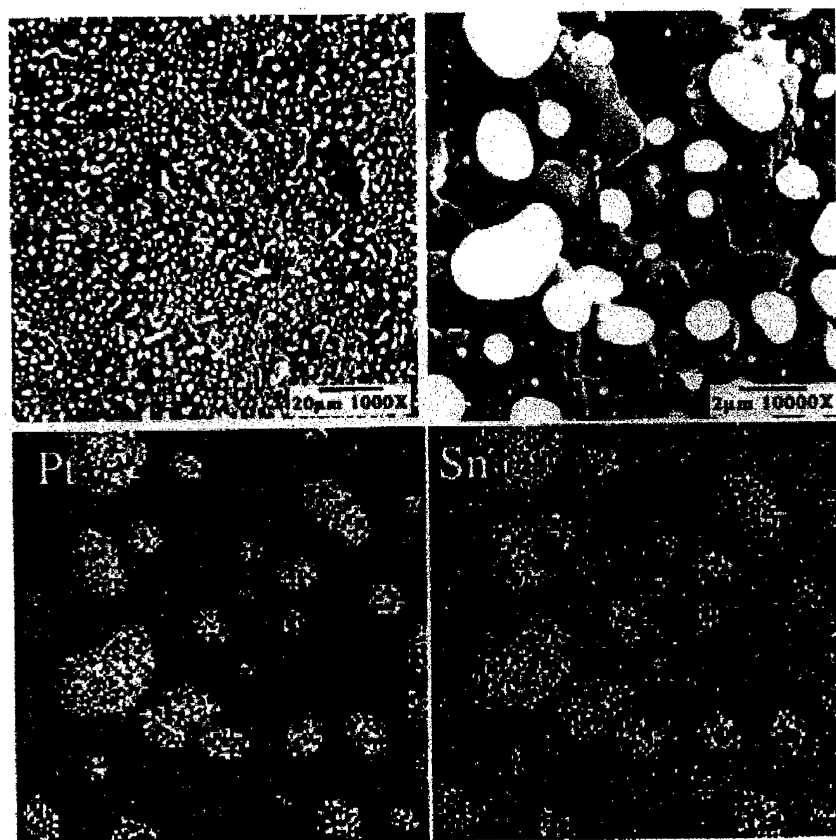
Figure 1



Pt
preheat
0.5
0.6
0.7
0.8
0.9
1
C_2H_4 selectivity
C_2H_6 conversion

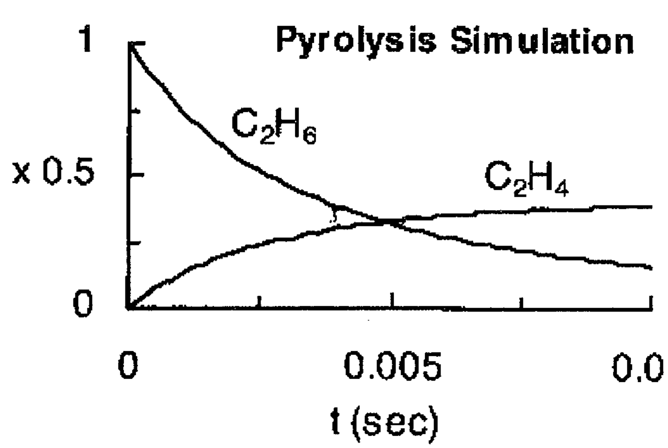
Pt-Sn/Al_2O_3 (after few hours)

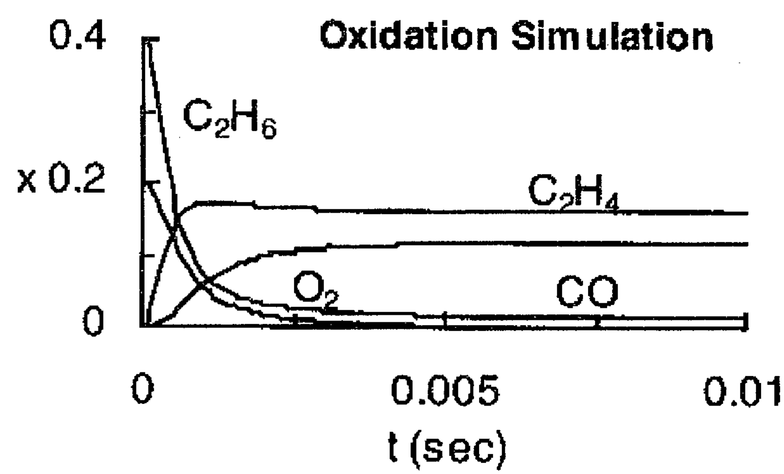
UNIVERSITY OF MINNESOTA



Homogeneous vs. Heterogeneous Chemistry

UNIVERSITY OF MINNESOTA





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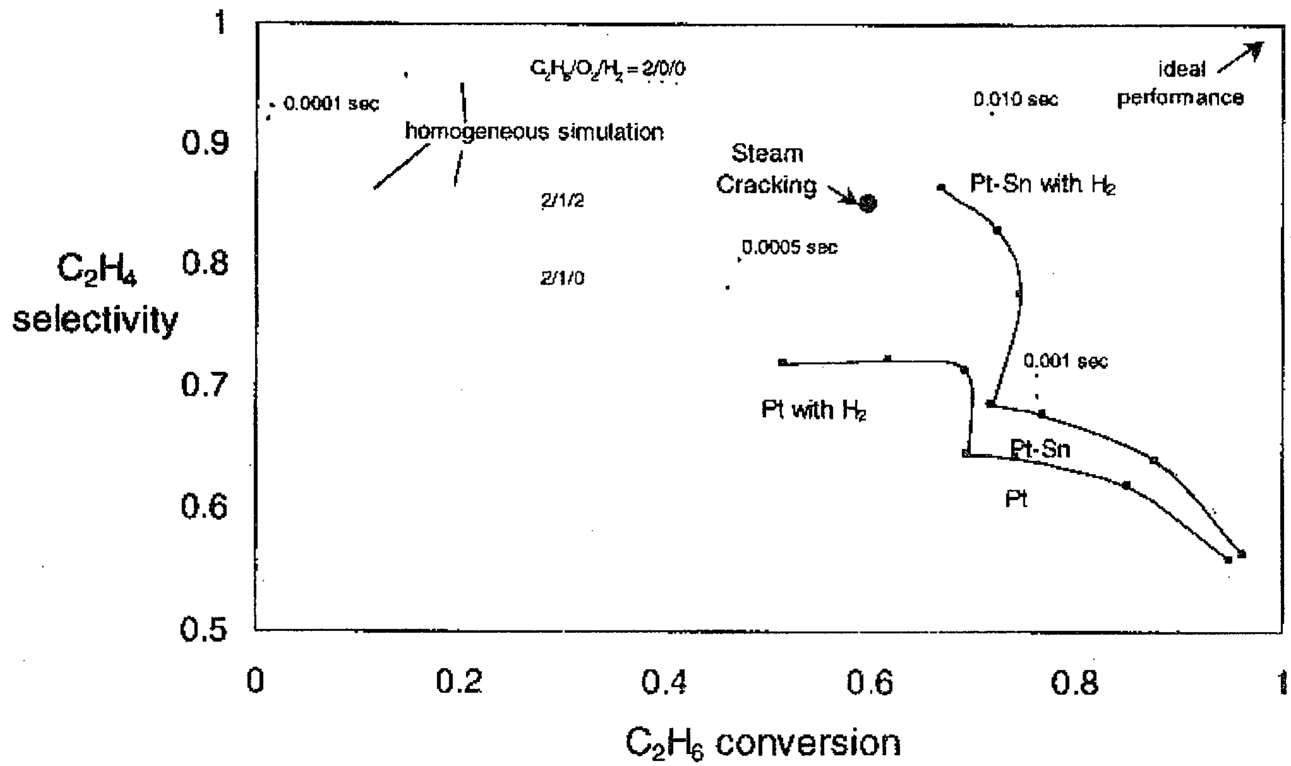
Homogenous vs. Heterogeneous Chemistry

UNIVERSITY OF MINNESOTA



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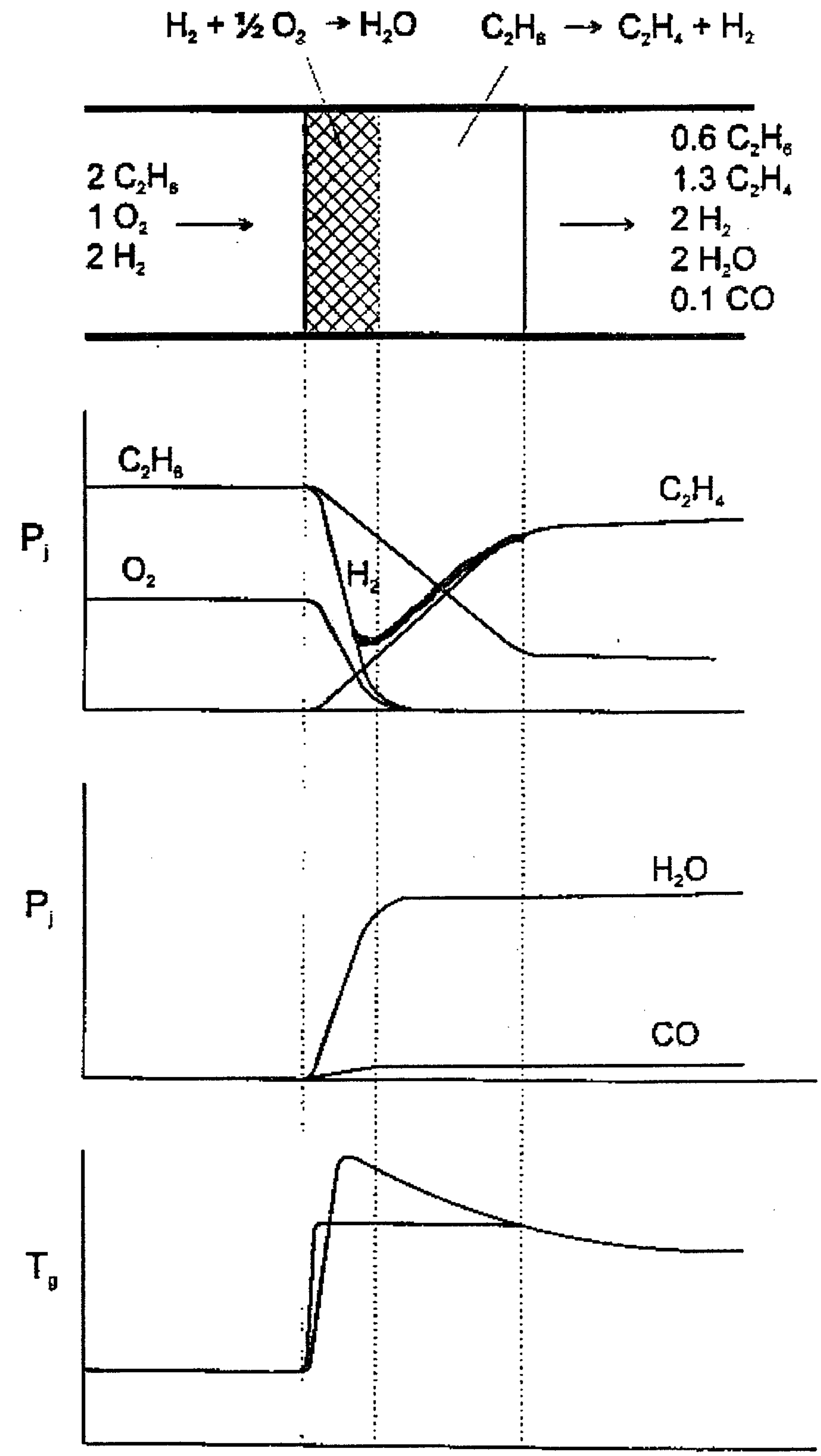

$H_2 + ½ O_2 \rightarrow H_2O$
$C_2H_6 \rightarrow C_2H_4 + H_2$
$2\ C_2H_6$
$1\ O_2$
$2\ H_2$
$0.6\ C_2H_6$
$1.3\ C_2H_4$
$2\ H_2$
$2\ H_2O$
$0.1\ CO$
P_j
C_2H_6
C_2H_4
O_2
H_2
P_j
H_2O
CO
T_g

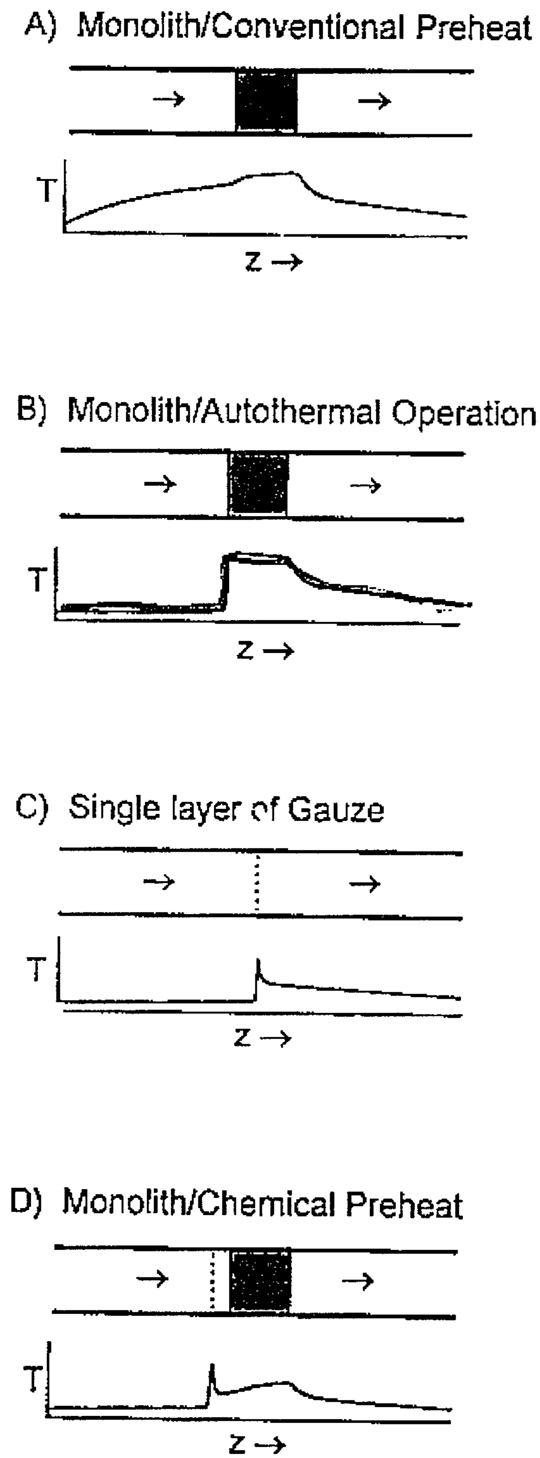
A) Monolith/Conventional Preheat
T
z →
B) Monolith/Autothermal Operation
T
z →
C) Single layer of Gauze
T
z →
D) Monolith/Chemical Preheat
T
z →

Fig. 1.

Millisecond Contact Time Reactor with Integrated Heat Exchange

Catalytic Radiant Burner and Heat Exchange Reactor

Jeremy M. Redenius
Department of Chemical Engineering and Materials Science
University of Minnesota

May 19, 1999

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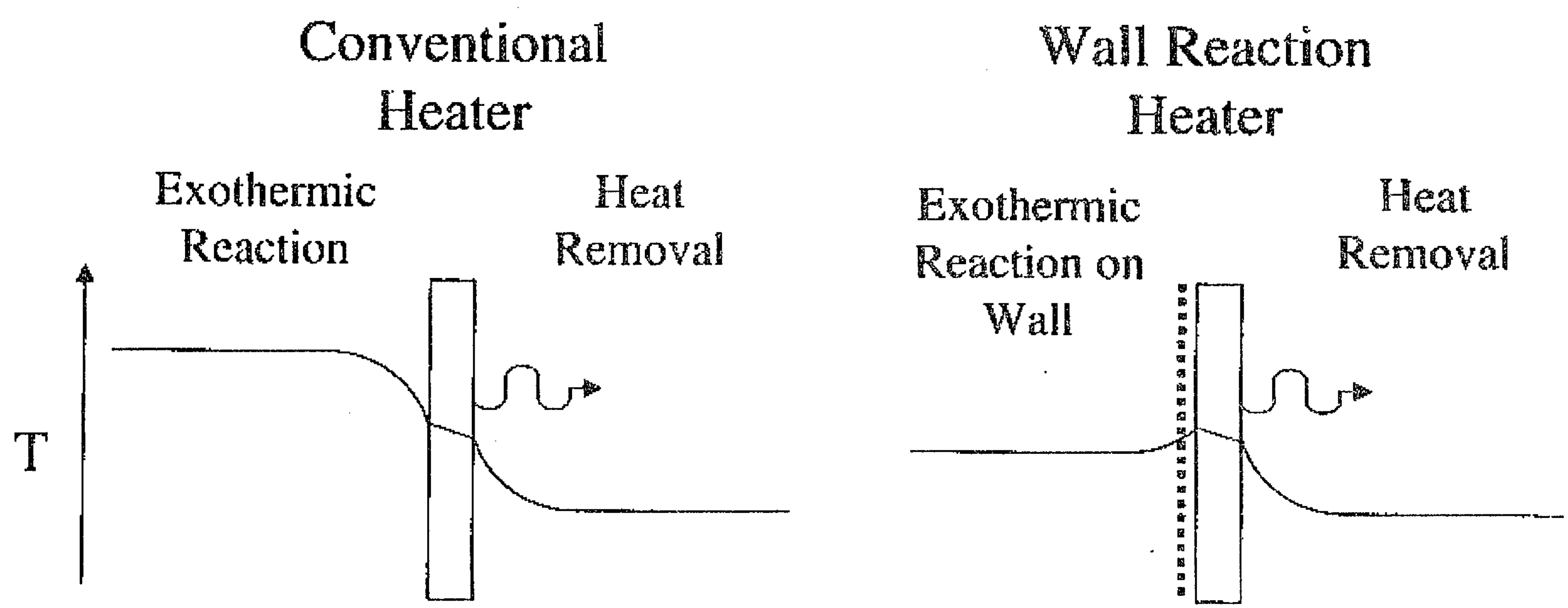
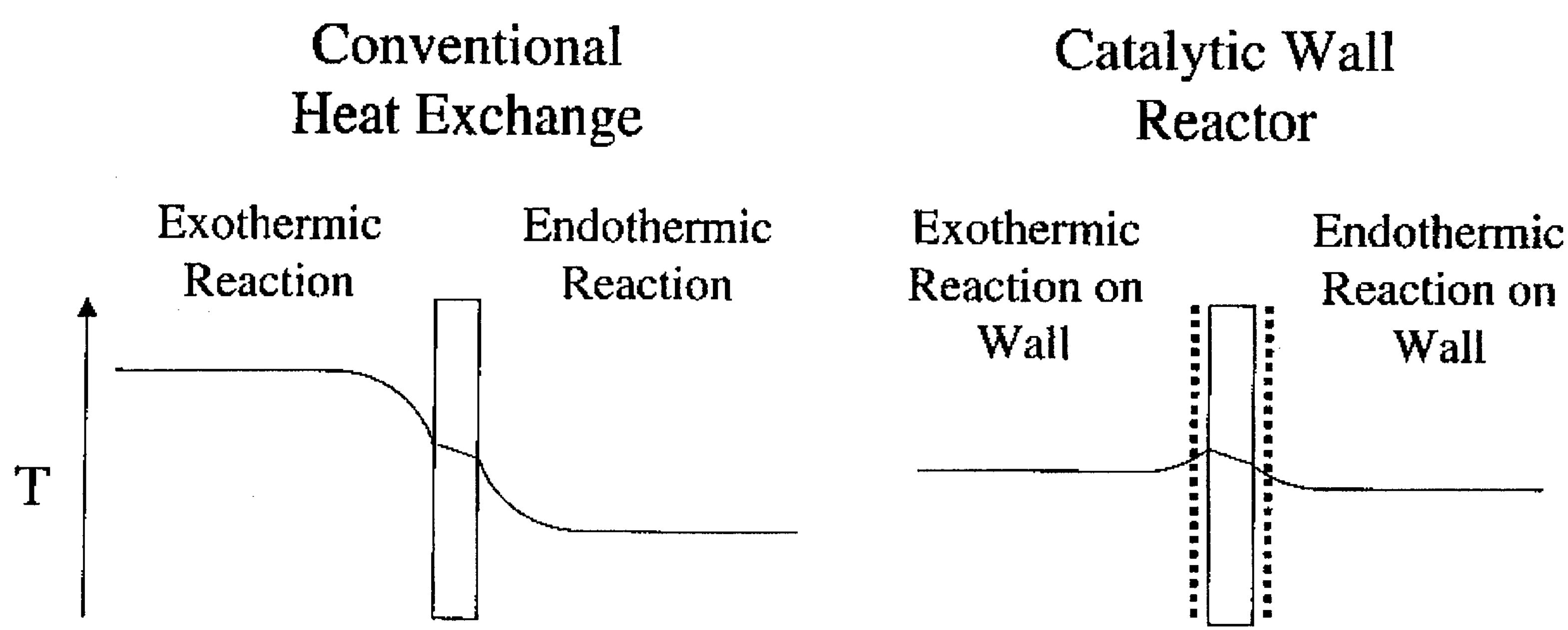
Catalytic Wall Radiant Heater

- Apply same technology to catalytic radiant heaters



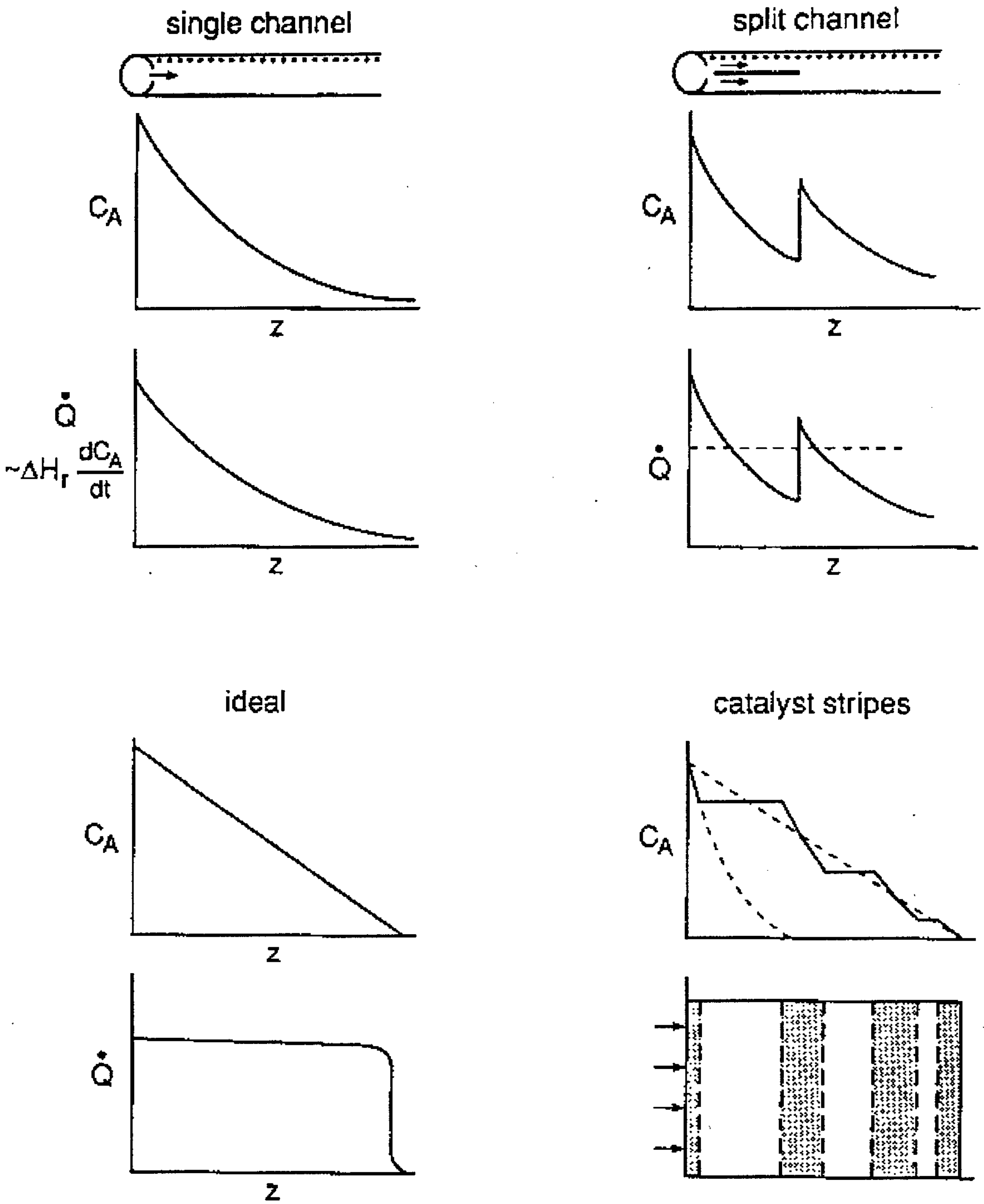
Eliminating Heat Transfer Limitations

- Move heat source close to heat sink

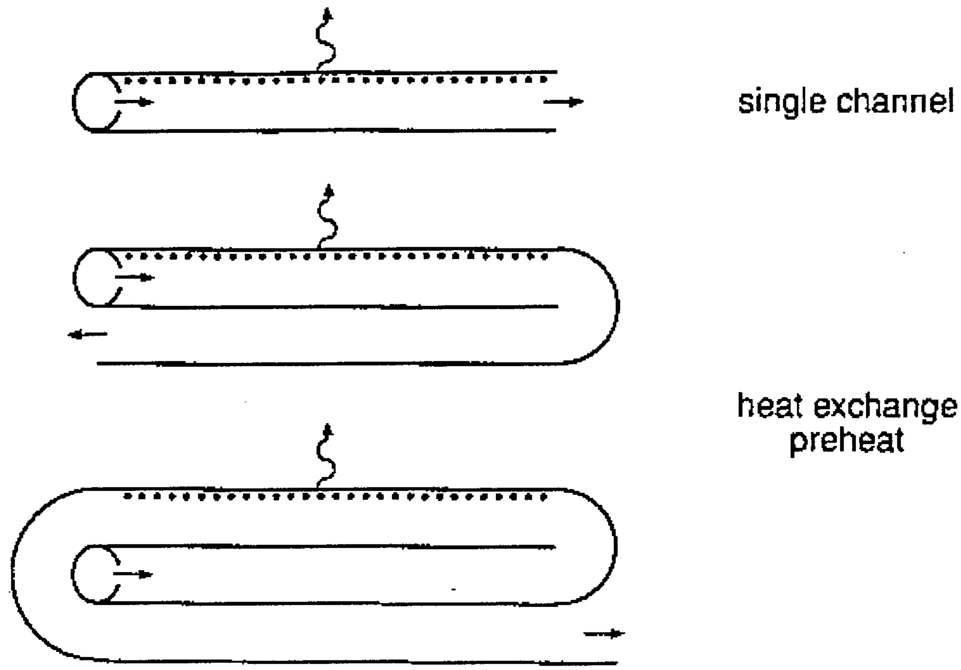


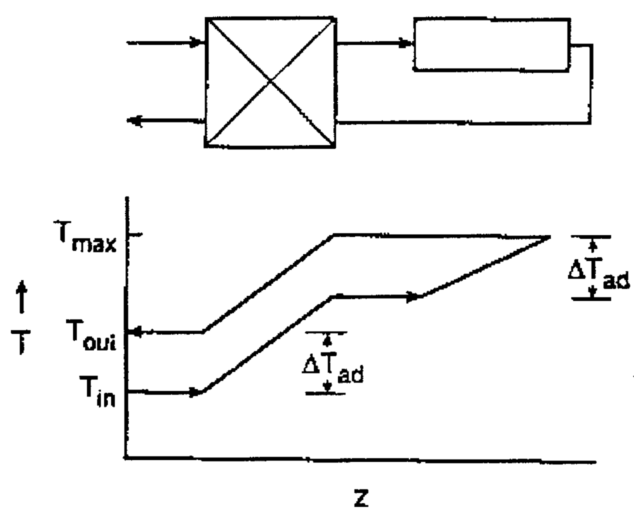
$$U = \left(\frac{1}{h_1} + \frac{l}{k} + \frac{1}{h_2} \right)^{-1}$$

Configurations for Uniform Temperature

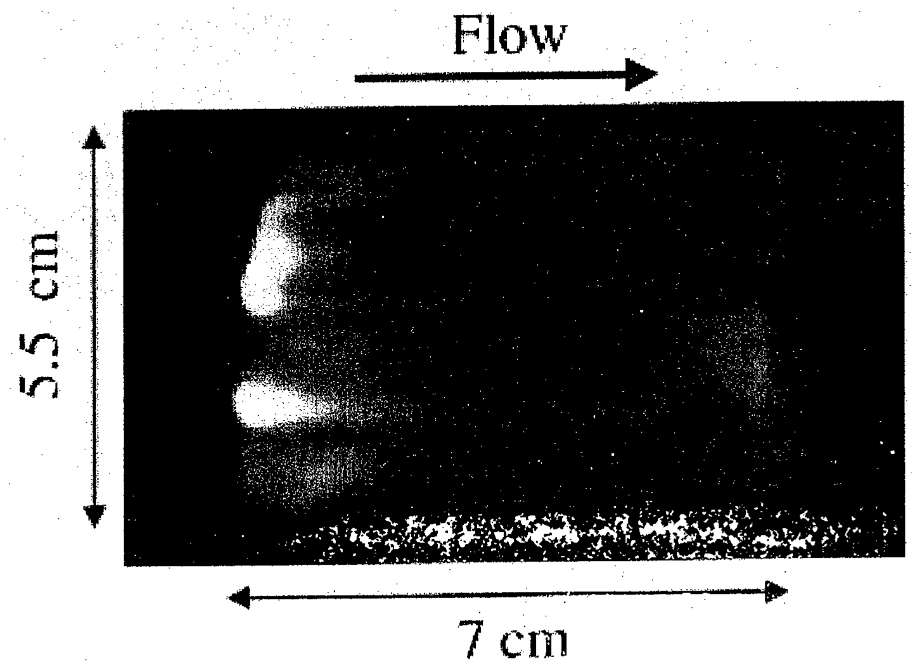


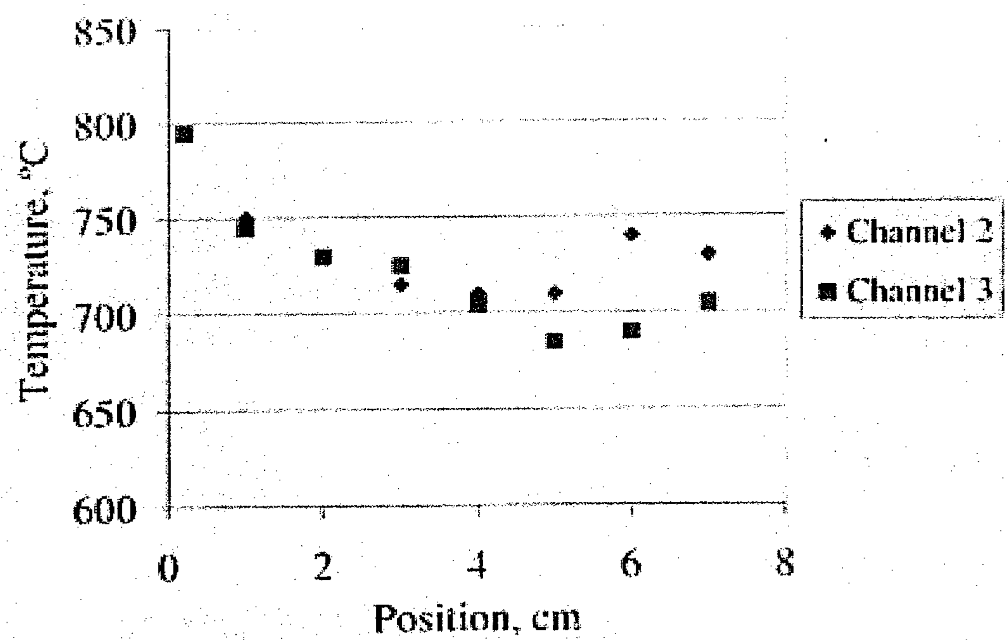
Heat Exchange Reactor



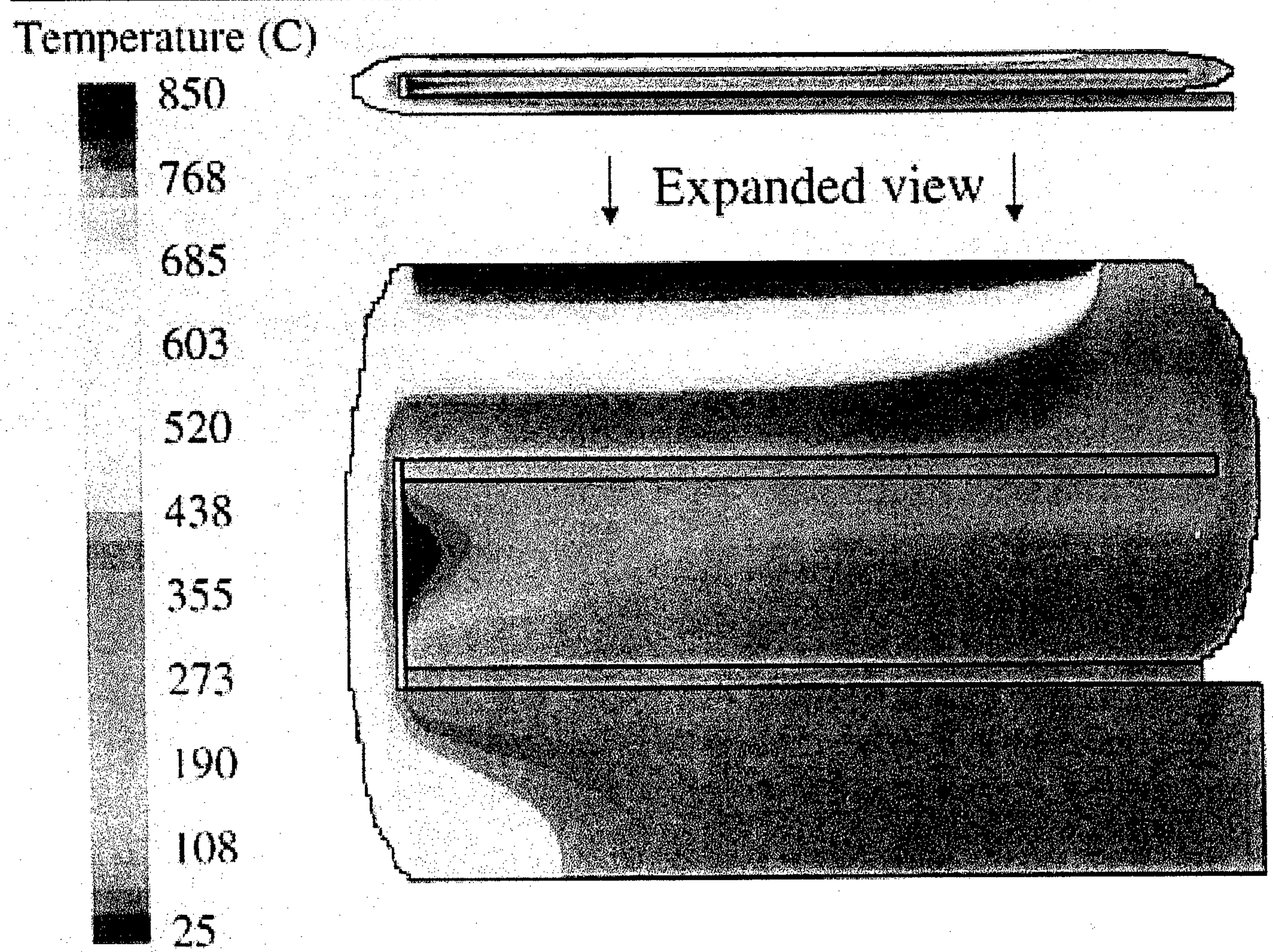


Radiant Surface

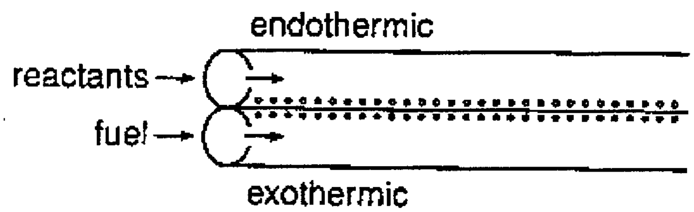




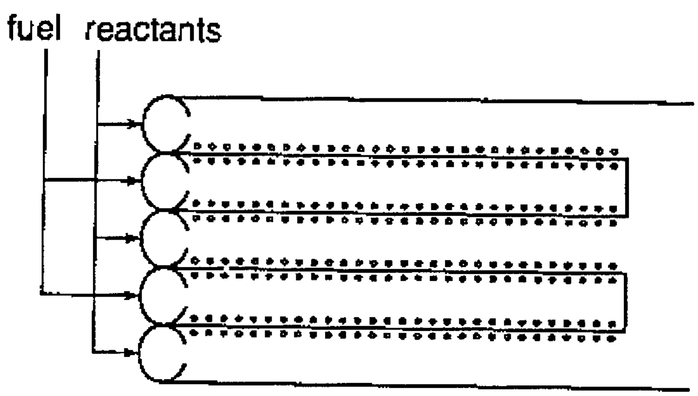
Bulk Gas Temperature



Catalytic Wall Reactor



catalytic wall reactor



manifold

X

CATALYST DESIGN

fast, exothermic, series reactions

$C_2H_6 \rightarrow C_2H_4 \rightarrow C_s \rightarrow CO$

remove O_2 quickly

- **Convective flow through catalyst**

  monolith
  channels
  no dead end pores

- **Short contact time**

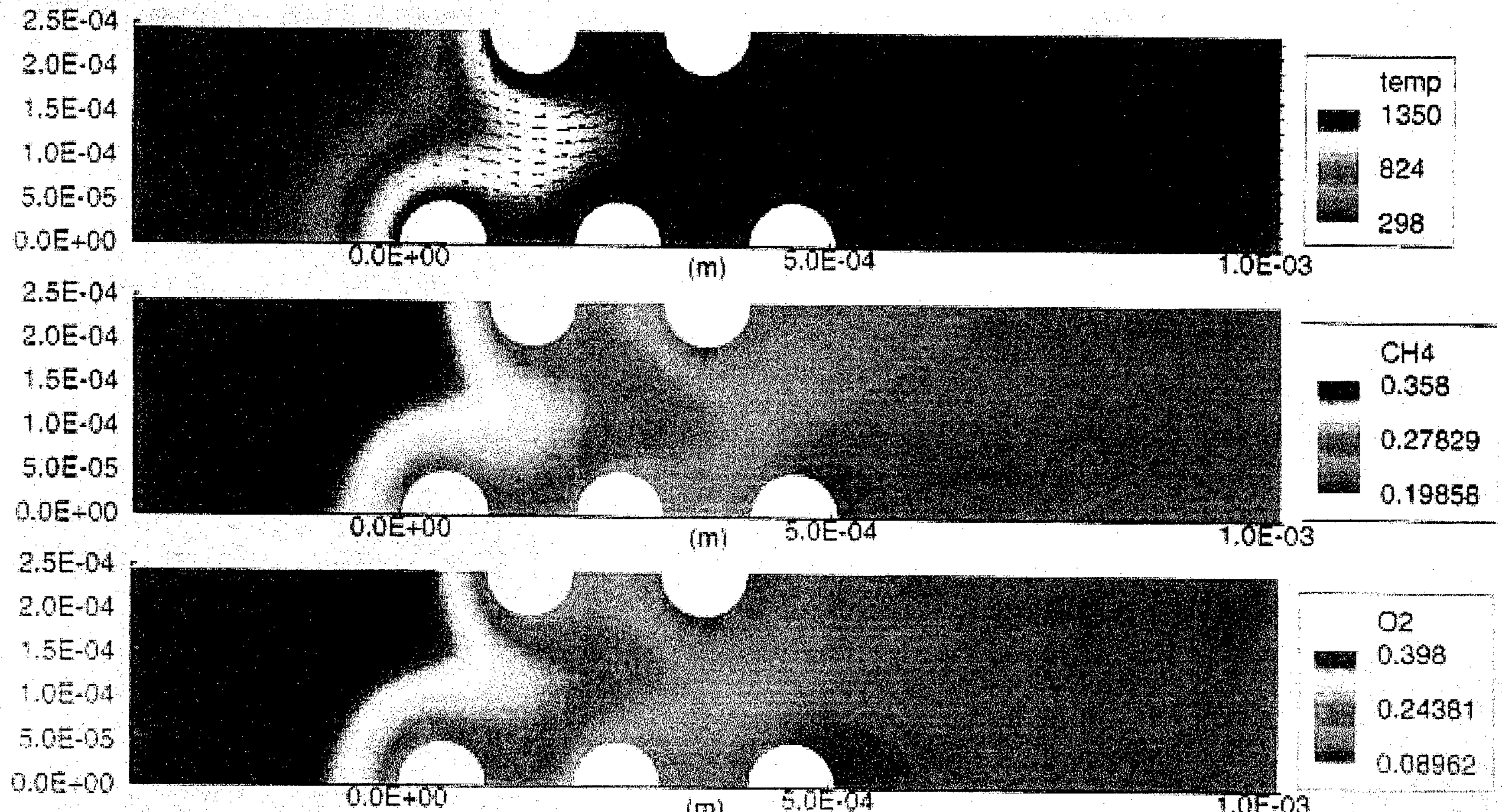
  remove products quickly
  reduce homogeneous reactions

- **High mass transfer**

  rough surfaces
  tortuous path

- **High heat transfer**

  backflow of heat
  prevent blowout


2.5E-04
2.0E-04
1.5E-04
1.0E-04
5.0E-05
0.0E+00
0.0E+00
(m)
5.0E-04
1.0E-03
temp
1350
824
298
CH4
0.358
0.27829
0.19858
O2
0.398
0.24381
0.08962

Radically Different Chemistry and Reactor

1. **400^oC hotter**
   $T \sim 1000^oC$

2. **10 to 1000 times faster**
   $\tau \sim 1$ millisecond

3. **Enormous throughput**
   1 ton/day from 100 grams of catalyst
   $GHSV \sim 10^6\ hr^{-1}$
   $TOF \sim 10^8\ sec^{-1}$

4. **Nonequilibrium products**
   1/2 of alkane should form graphite
   olefins and oxygenates should not form

5. **Surface area not important**
   identical results with 0.1 to 20% metal
   want channels, not pores

6. **Chemistry cannot be dissected**
   many steps not measurable individually
   homogeneous steps?

Summary

Ethylene from Ethane by Partial Oxidation

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O$$

feed 2/1/2 $C_2H_6/O_2/H_2$
85% selectivity at >70% conversion using PtSn with H_2
less than 1 millisecond residence time
thermodynamics predicts <1% ethylene, mostly CO and CH_4

Mechanism is catalytic

$$H_2 + O_2 \rightarrow H_2O$$

followed by

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Feed 2/1 H_2/O_2 mixture
nonflammable with ethane present
ethane enters into homogeneous chemistry and quenches

All H_2 recovered with 2/1/2 feed

CO_x decreases from 25% without H_2 to <5% with H_2
completely shut of C oxidation channel even at 1000°C
entropy argues that high selectivity only possible at low

Production of Oxygenates in Single-Gauze Reactors

Ryan P. O'Connor

Department of Chemical Engineering and Materials Science
University of Minnesota
20 May 1999

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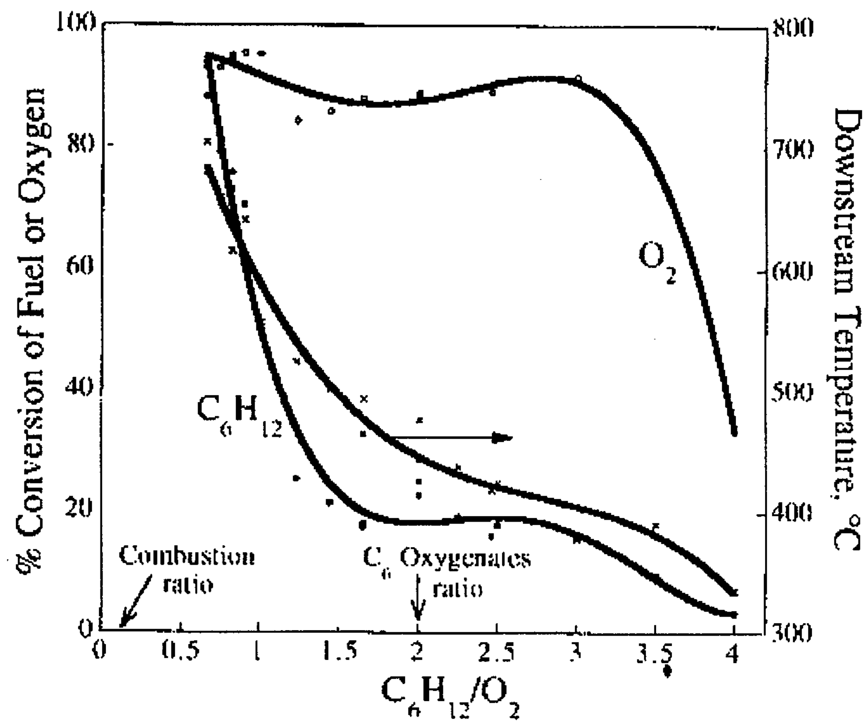
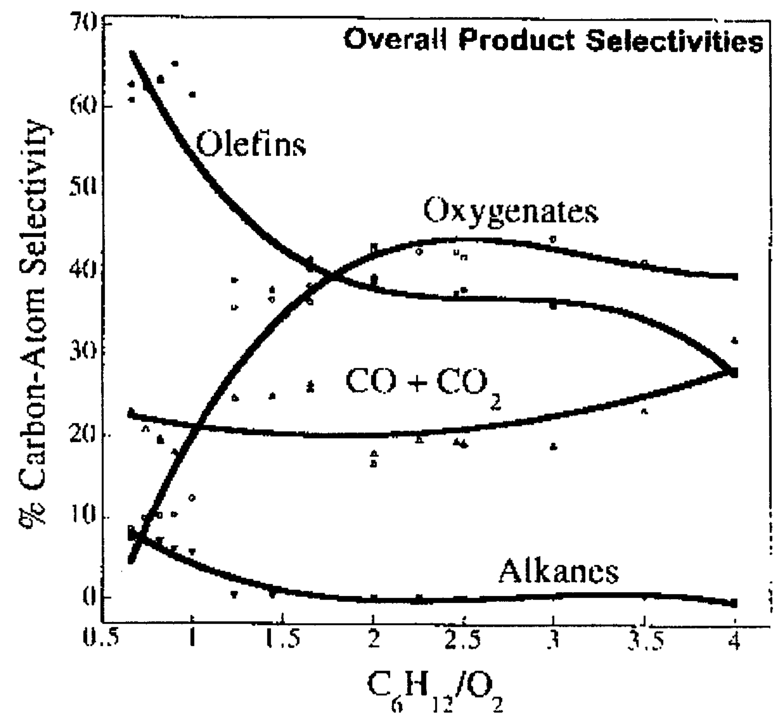
C_6H_{12} Partial Oxidation: Effect of Fuel–Oxygen Ratio





90% Pt–10% Rh 40-mesh single gauze

2.5 SLPM feed, 30% N_2 dilution, T_0 = 200°C, and P = 3 psig

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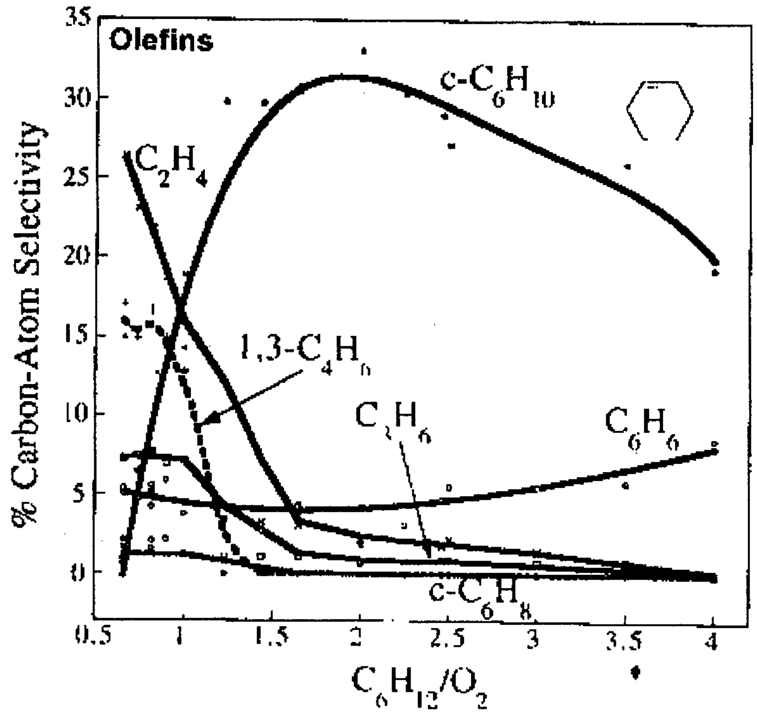
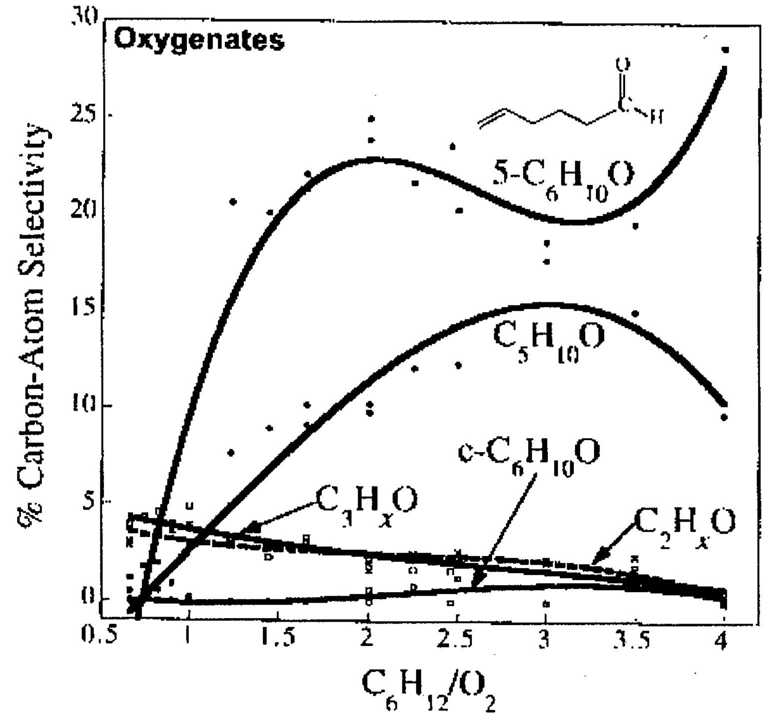
C_6H_{12} Partial Oxidation: Effect of Fuel–Oxygen Ratio

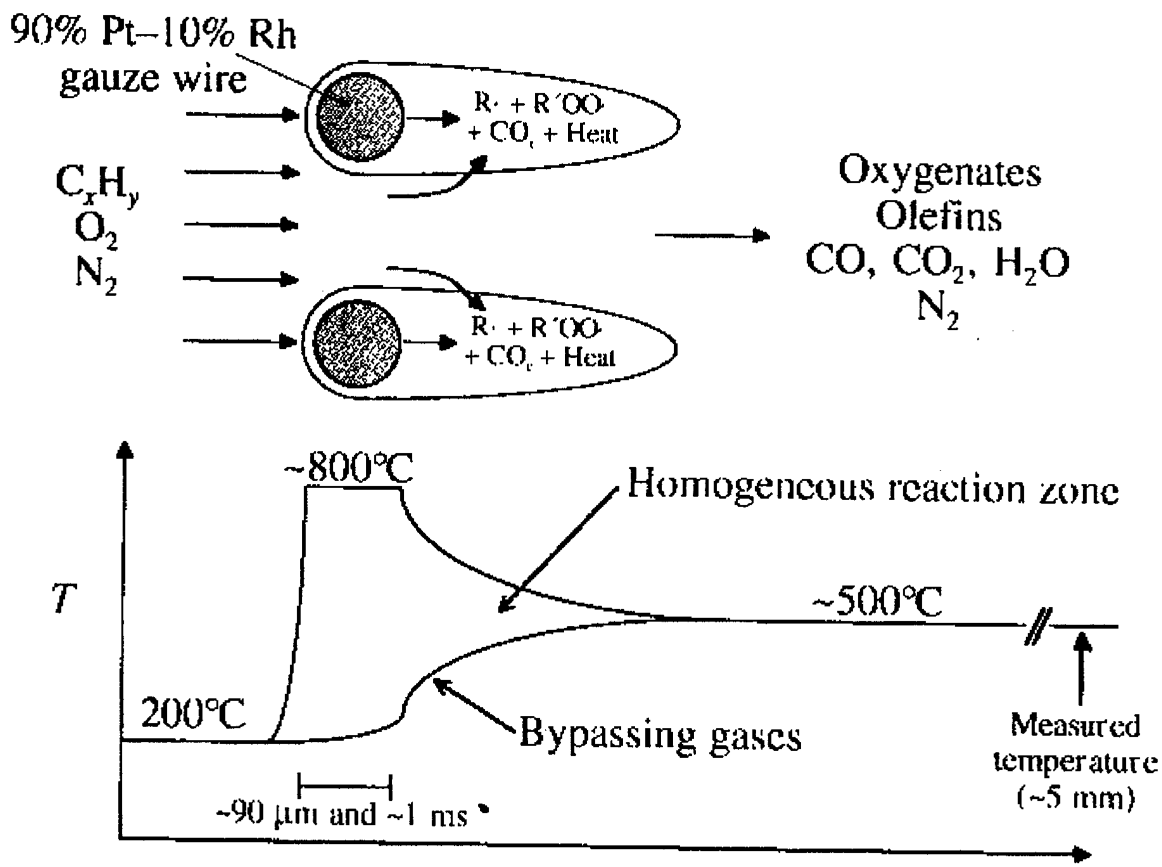




90% Pt–10% Rh 40-mesh single gauze

2.5 SLPM feed, 30% N_2 dilution, $T_0 = 200°C$, and $P = 3$ psig

Single–Gauze Catalyst



★ Surface-assisted homogeneous reaction
★ Rapid quenching → non-equilibrium products (oxygenates)

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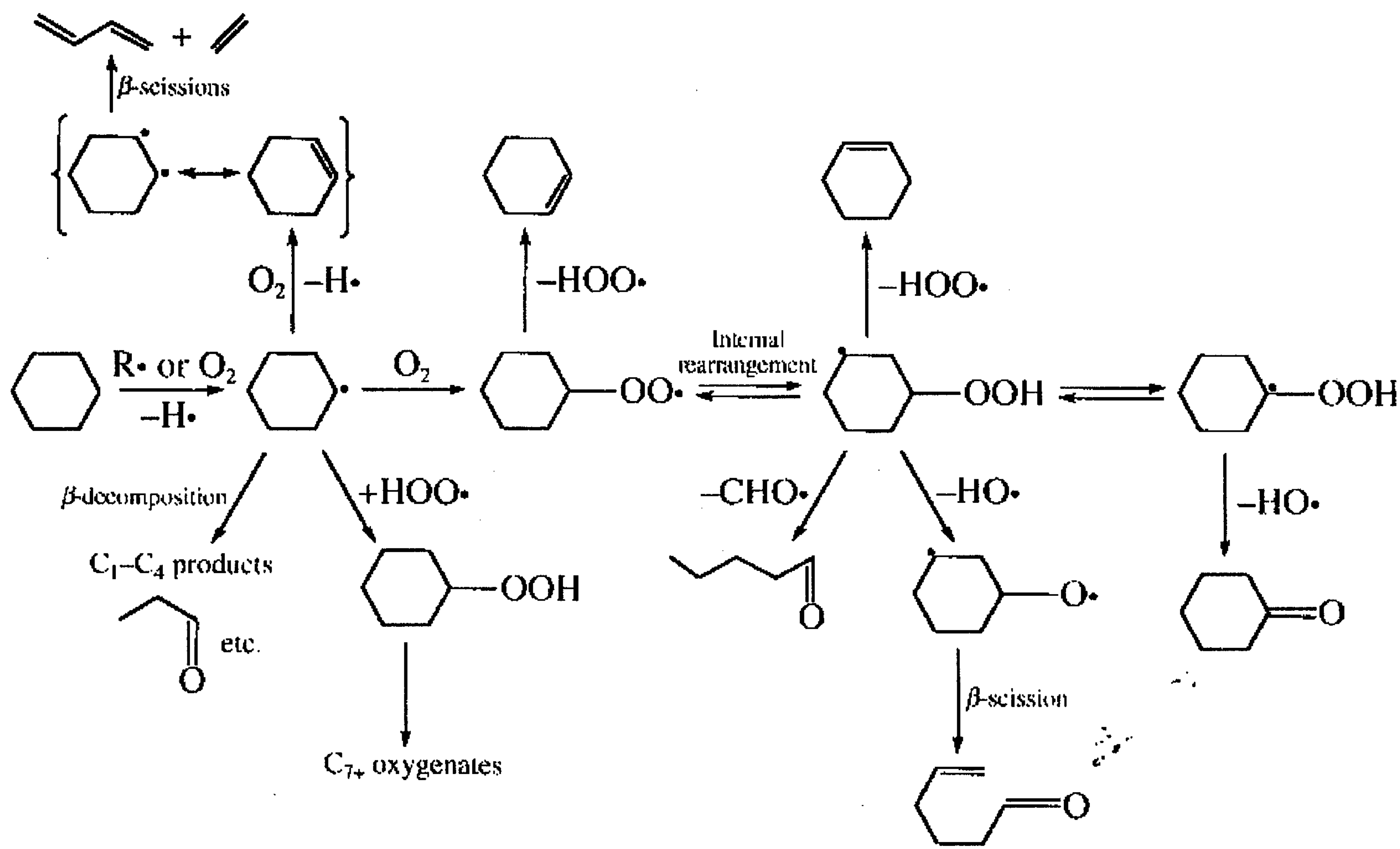
Surface-Assisted Homogeneous Pathways



Summary of Results for Cyclohexane Partial Oxidation

➢ Three main regimes of operation (Pt–10% Rh single gauze):

★ $C_6H_{12}/O_2 < 0.7$: flames can develop (large amounts of CO_x)
★ $C_6H_{12}/O_2 = 0.7–1$: ~60% olefin selectivity (mostly $C_2H_4 + C_4H_6$)
★ $C_6H_{12}/O_2 > 1$: 5-hexenal, pentanal, and cyclohexene dominate

➢ Oxygenate production is favored by:

★ Cyclohexane–oxygen ratio of 2–3 (selectivity up to 50%)
★ Intermediate dilution: 20–30% N_2 in feed (moderate effect)
★ Higher flow rates: ~2.5 SLPM best in 1–3 SLPM range
★ Lower inlet temperatures: ~100°C (higher T_0 promotes olefins)

➢ Pt–10% Rh single gauze versus Pt-coated foam monolith:

★ O_2 conversions higher over single gauze by ~10%
★ CO_x selectivities similar (surface mechanisms comparable)
★ No C_5 or C_6 oxygenates in foam-monolith reactor

COMBUSTORS FOR MICRO HEAT ENGINES

Professor Ian A. Waitz

Massachusetts Institute of Technology

Presenting the work of

Amit Mehra, Xin Zhang, Chris Cadou, Arturo Ayon, Steve Lukachko & Jinwook Lee

Microchemical Systems and Their Applications Workshop

ARO/DARPA

June 16-18, 1999

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OUTLINE

- Brief overview of the MIT MicroEngine Project
  - Combustion requirements for heat engines
- Review of challenges and opportunities for microscale combustion
  - Homogeneous gas phase combustion
  - Catalytic combustion
- Summary, key issues and needs, conclusions

THE MIT MICROENGINE PROJECT

- **Premise:**
  - Advances in microfabrication of silicon and other materials enable the development of a new class of power-MEMS
- **Applications:**
  - Gas turbine engines
  - Electrical generators
  - Refrigerators
  - Turbo-pumps, compressors, blowers
  - Rockets
  - Other heat engines
- **Principal figure of merit:**
  - Power density (W/m^3)
  - ~ 1/length-scale

MICRO ENGINE "DEVELOPMENT" ORGANIZATION

Ehrich
Senturia

IPMT
Epstein - Chief Eng.
Jacobson - Asst. Chief Eng.
Schmidt
Spearing
Waitz
Protz

Systems, Integration, & Requirements
Epstein
Jacobson
Protz
Frechette‡

Aero
Tan*
Jacobson
Youngren
Cadou
Frechette‡
Khan
Gong

Recuperator
Brisson*
Sullivan

Mat'ls & Structures
Spearing*
KS Chen
Lohner
Miller
Walters
Ye
Huang (LL)

Bearings & Dynamics
Breuer*
Ehrich
Orr
Piekos
Lin
Savoulides
Jacobson

Combustion
Waitz*
Mehra
Lee
Lukachko
Cadou

Electromechanics
Lang*
Umans‡
Livermore
Nagle‡
Warren
TBA

Fabrication
Schmidt*
Ayon
Ghodssi‡
Lin
DZ Chen
Khanna
McClure
Zhang‡
Warren
TBA
TBA, TBA (LL)

Test & Inst.
Jacobson*
Protz
Breuer
DZ Chen
TBA

Packaging & Installation
Spearing*
Retherford (LL)
Harrison
London

Controls & Accessories
Epstein*†
Protz
Umans
Paduano
Liu
TBA

*Lead (LL) Lincoln Lab † Acting
‡ Focussed on motor-compressor
Full-Time Staff/Post Doc Grad Student

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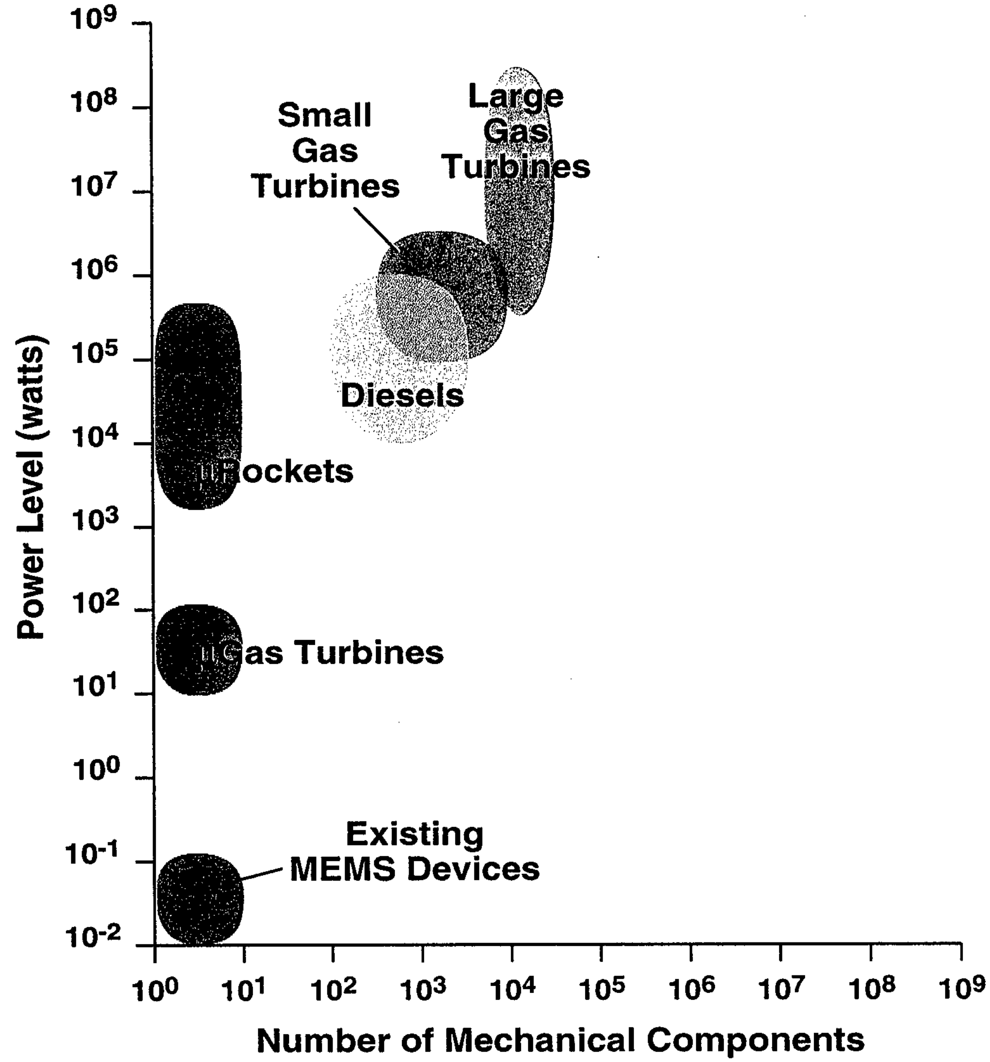
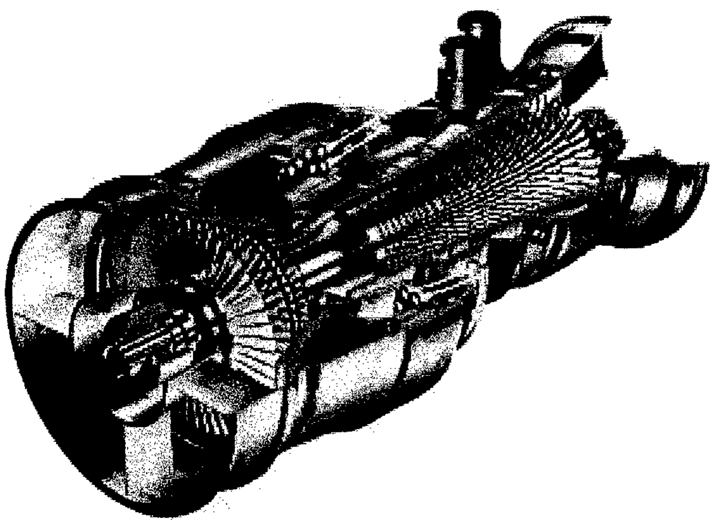
MEMS POWER


Power Level (watts)
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
Small Gas Turbines
Large Gas Turbines
Diesels
μRockets
μGas Turbines
Existing MEMS Devices
10^0 10^1 10^2 10^3 10^4 10^5 10^6 10^7 10^8 10^9
Number of Mechanical Components

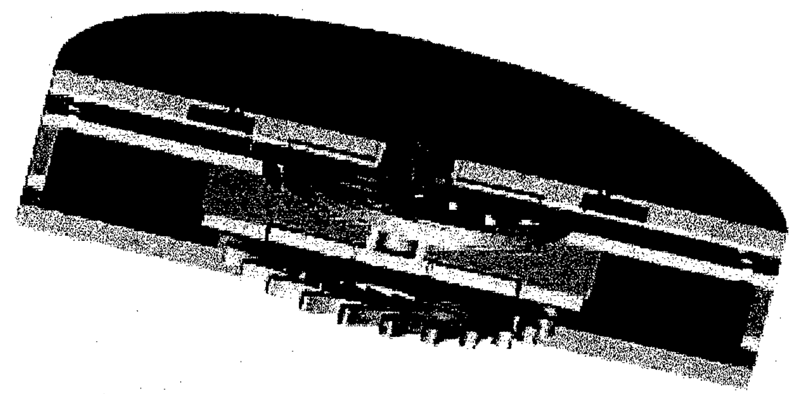
"MACRO" vs. "MICRO" GAS TURBINES

"MACRO"



10,000 parts
Inlet dia = 2 meters
Airflow = 500 kg/sec
Weight = 400 tons
Power output = 150 MW
Cost ~ $300/KW

"MICRO"



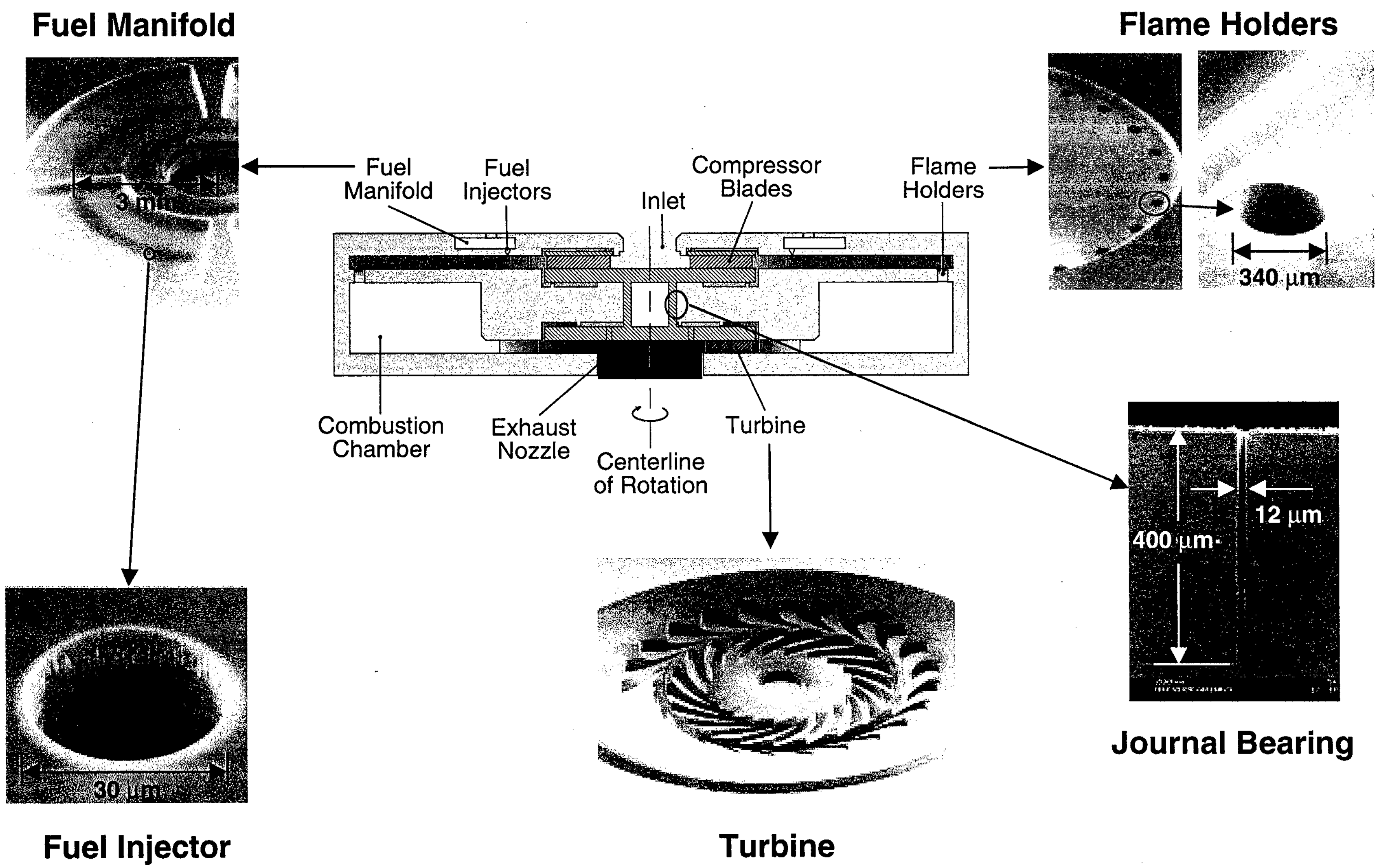
2 parts
Inlet dia = 2 mm
Airflow = 0.25 g/sec
Weight = 1 gram
Power output = 50 watts

HIGH POWER DENSITY THERMODYNAMIC CYCLES
- Physical Requirements -

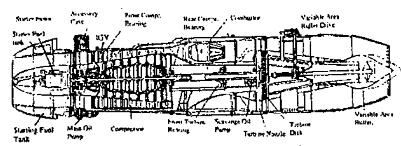
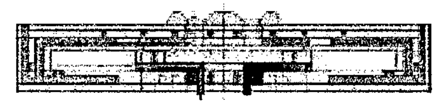
- High peak cycle temperatures (1200 ~ 1700°K)
  - High temperature materials
- High peripheral speeds (400 - 600 m/s), thus
  - Highly stressed rotating parts (100's MPa)

    [Fluid & electric power density $\propto$ (Tip speed)^2 $\propto$ Stress]
- Low friction bearings
- Reasonable component efficiencies
  - Close tolerances (1 μm)

MICROENGINE FABRICATION PROGRESS



TURBOJET ENGINE COMPARISON

			
Engine	JUMO 004 (1939)	J-85[t] (1954)	Demo Micro (1999)
Airplane	Me-262	T-38, F-5	MAV
Engine Dia.	31”	18”	0.8”
Thrust	2000 lbs	2950 lbs	2500×10^{-6} lbs
Thrust/Wt.	1.2:1	7.3:1	5.5:1
Thrust/Airflow (lb/lb/sec)	43	67	30
TSFC* (lb/hr/lb)	1.4	1.0	1.4
Turbine Inlet Temp.	1430°F	1715°F	2421°F
Overall Pressure Ratio	3:1	7:1	2:1

* Thrust specific fuel consumption
[t] w/o afterburner

μENGINES ARE NOT SCALED-DOWN BIG ENGINES

Physics Intrinsic to Small Devices	Current Technology Limits
Fluid viscous effects up	2-D “extruded” shapes preferred
Surface area to volume high	Etching depth & aspect ratio
Short heat conduction paths	Number of layers (~10+)
Chemical reaction times const.	Most fab tech applies mainly to Si
Many materials are stronger	Assembly and packaging

MIT MICROENGINE PROJECT STATUS

- Static structure preliminary testing complete
  - Successful fab/construction/etc.
  - Second and third versions coming soon
- Micro-bearings operated to 500,000+ rpm
  - 1,200,000 rpm design speed
  - Greater control over fab tolerances required
- Turbomachinery performance worse than expected due to heat transfer effects
  - But sufficient to close cycle
- First H_2 demo engine in ‘00
  - No apparent physical barriers to successful demonstration
- Parallel efforts ongoing
  - Liquid fuels, packaging, silicon carbide technologies, electrical and magnetics
  - Micro Air Vehicle airframe, and guidance and control
  - Micro-rockets

MICROCOMBUSTOR DEVELOPMENT

- Functional requirements
  - Convert chemical energy to thermal + kinetic energy w/high efficiency
  - Low total pressure drop
  - Given cycle/component performance
  - Ignition, operability, ..., etc.
- Constraints
  - Materials/structures
  - Fabrication
- Desire high power density (W/m^3)
- Scaling issues introduce new challenges and opportunities

POWER DENSITY

- Maximum space heating rate (hydrocarbon-air)
  - $45 MJ/kg_{HC} \Rightarrow 3 MJ/kg_{HC+air} \approx 3 MJ/m^3$
  - For $\tau_{res} = 1 \times 10^{-5}$ s

    heating rate = 3×10^5 MW/m^3-atm
- Current "macro" gas turbine combustors

  heating rate $\approx 4 \times 10^1$ MW/m^3-atm
- MIT 0.07cm^3 silicon microcombustor (150W at 1 atm)

  heating rate = 2×10^3 MW/m^3-atm

MEMS POWER DENSITY

Device	Power Density (MW/m^3)
Micro lithium batteries	0.4
Micro solar cells	1
Micro-electric motors	1.7
Microreactors (silicon)	20
Large-scale combustors	40
Micro channel reactors	150
Micro-magnetic motors	200
Silicon microcombustors	2000

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CHEMICAL KINETICS / RESIDENCE TIME CHALLENGES

- Small volume + high flow rates $\Rightarrow$ <u>High power density</u>
- Residence time $\propto$ pressure $\times$ volume / mass flow rate
  - We have low pressure, small volume, high mass flow rates
- Residence time required is set by chemical reaction rate
- Kinetic rates $\neq$ fcn[size] (gaseous reactions)
  - $\tau_{chem} \Rightarrow \tau_{res} \approx 1\text{x}10^{-5}\text{s}$ to $1\text{x}10^{-6}\text{s}$ (p=1 atm)

THE POWER DENSITY OF A MICROCOMBUSTOR IS LIMITED BY THE REACTION RATE OF THE FUEL

HEAT TRANSFER CHALLENGES

- Large surface area-to-volume ratio (~ 1/length-scale)
  - 500 m^{-1} vs. 3-5 m^{-1} for a large-scale device
  - Reduces combustor efficiency
  - Quenches reactions and radicals at the walls
  - Increases chemical reaction times

- Heat conduction paths short (~ length-scale)
  - Low Biot number
  - Heat transfer rates set by convection, structure is nearly isothermal

COUPLING BETWEEN THE FLUID DYNAMICS, HEAT TRANSFER AND CHEMICAL KINETICS IS MORE PRONOUNCED FOR MICROCOMBUSTION SYSTEMS

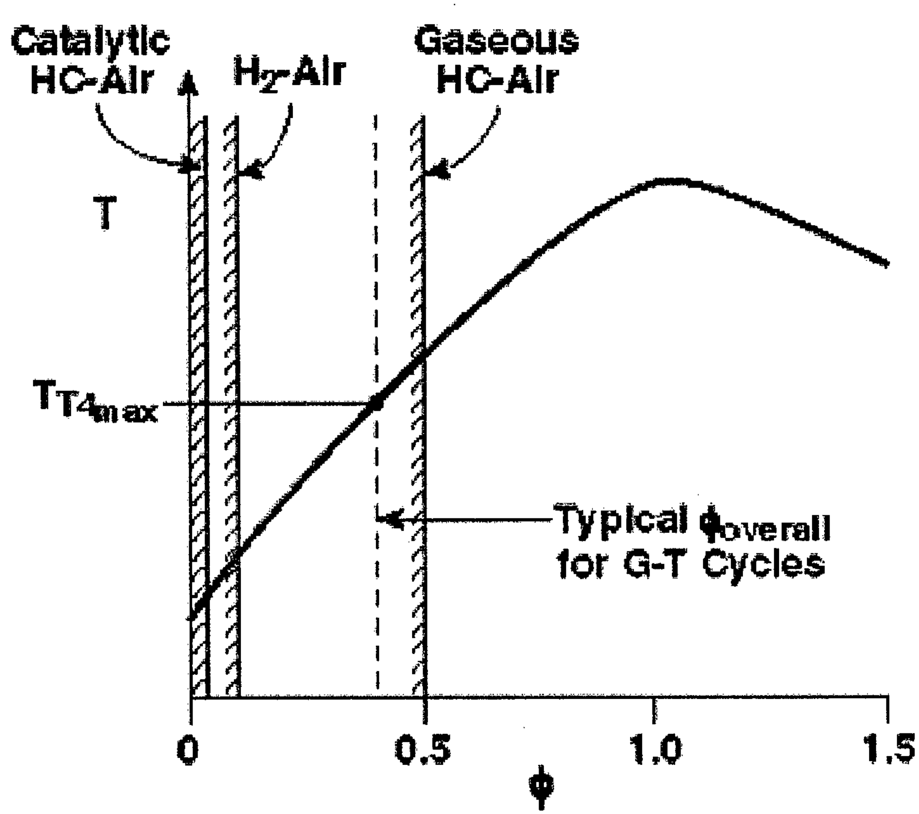
FABRICATION CHALLENGES

- Silicon fabrication limited to rudimentary 3-D geometry, creep concerns limit wall temperatures to below 900K
  - Alternative materials limited
  - Chemical kinetics demand temperatures higher than 900K for stable and efficient combustion
  - Need to cool the walls or split the combustor into two zones $\Rightarrow$ decrease efficiency or increase fabrication complexity

THE EFFICIENCY OF A MICROCOMBUSTOR IS LIMITED BY THE FABRICATION AND MATERIAL CONSTRAINTS OF SILICON

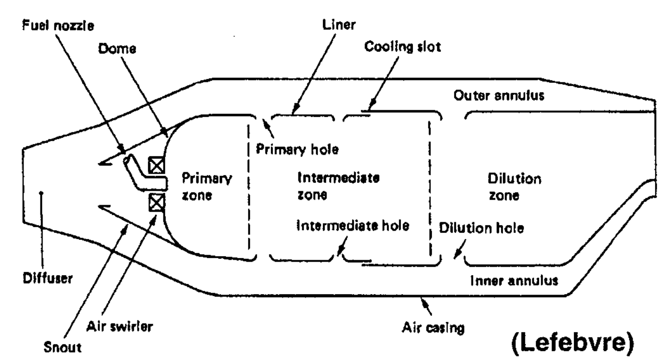
HYDROCARBON FLAMMABILITY LIMITS

- Cycle/material requirements + hydrocarbon flammability limits mandate a two-zone process for many applications



$$h\dot{m}_f = \dot{m}_a C_p \left(T_{T_4} - T_{T_3}\right)$$

Primary Zone
(Stoichiometric, high T)
+
Dilution zone



(Lefebvre)

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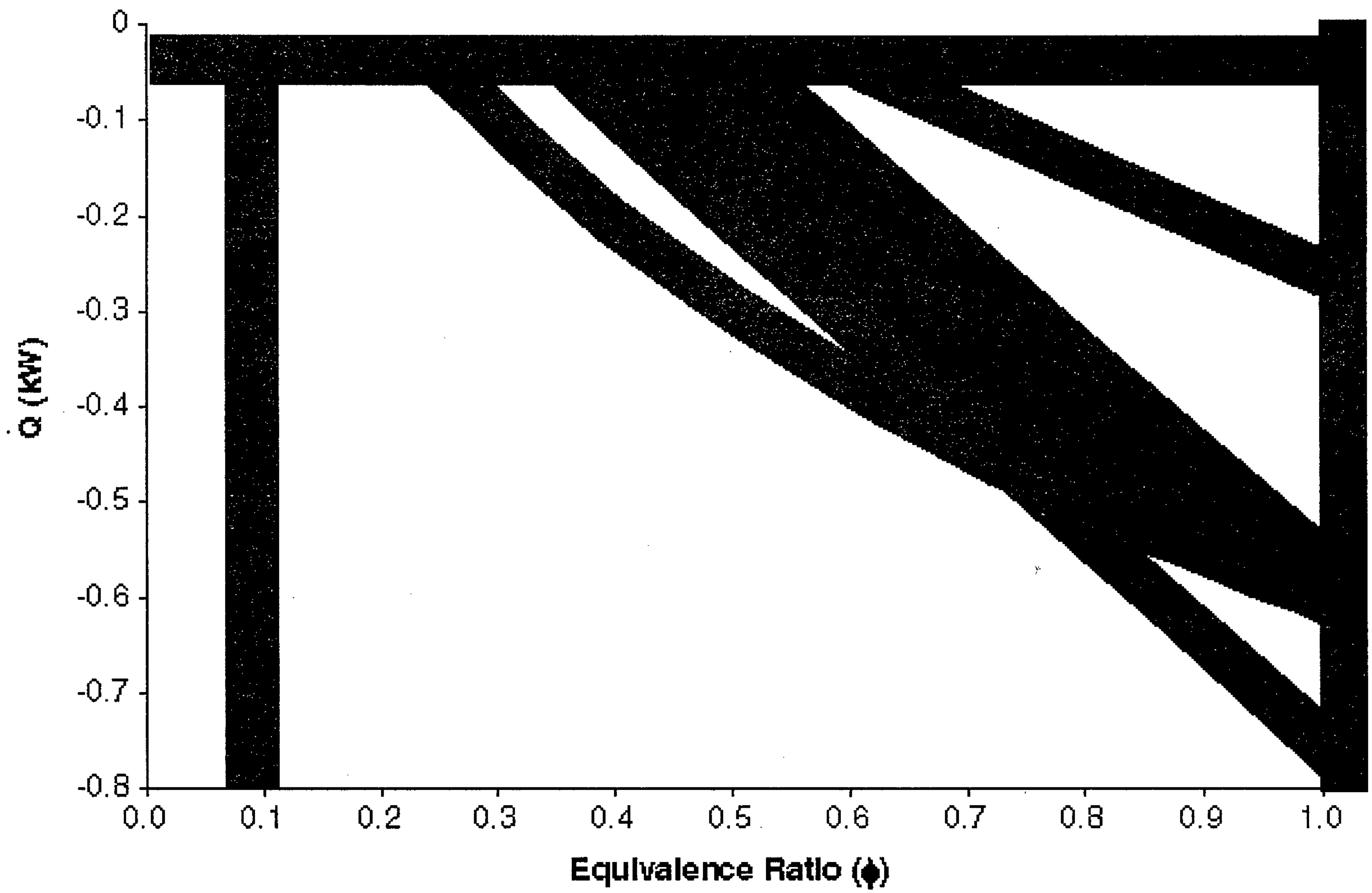
OTHER FACTORS

- Viscous effects more important
  - Low Reynolds number $\Rightarrow$ laminar mixing and combustion processes
- Some materials stronger
- System constraints more stringent
  - All other components pushed to extreme as well
- Effective diagnostics do not exist
  - Must be built into test devices
- Different regime for numerical simulations
  - Traded turbulence for coupled heat transfer + reacting flow (gas phase and surface chemistry)

MICROCOMBUSTOR STRATEGIES

- Increase combustor volume relative to engine
  - 50x $\Rightarrow$ 0.5 to 1 ms residence time
- Lean, premixed
  - ϕ " 0.4
  - Whole process at $T < T_{max\text{-}material}$ (no wall cooling necessary)
  - Need wide flammability envelope
    - H_2-air
    - Hydrocarbon-air + surface catalysis
- Or ϕ " 0.8 hydrocarbon + careful thermal design + higher temperature materials

DESIGN SPACE FOR HYDROGEN-AIR
(P = 2.7 atm, T_i = 700 K)



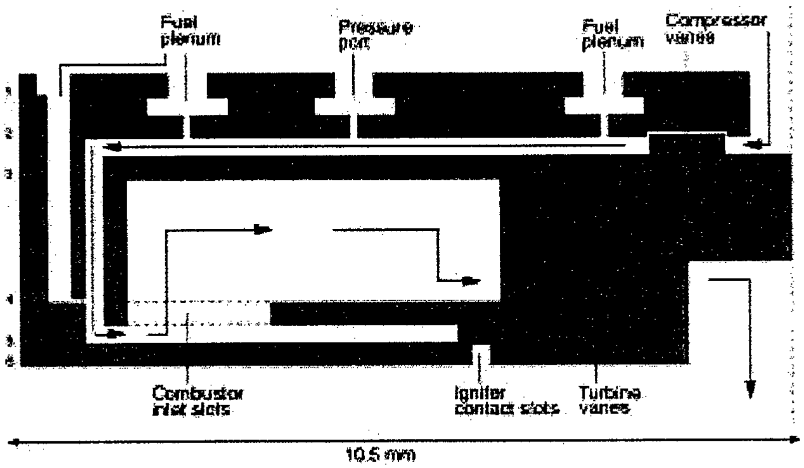
INTEGRATION WITH DEVICE
Static Structure Objectives

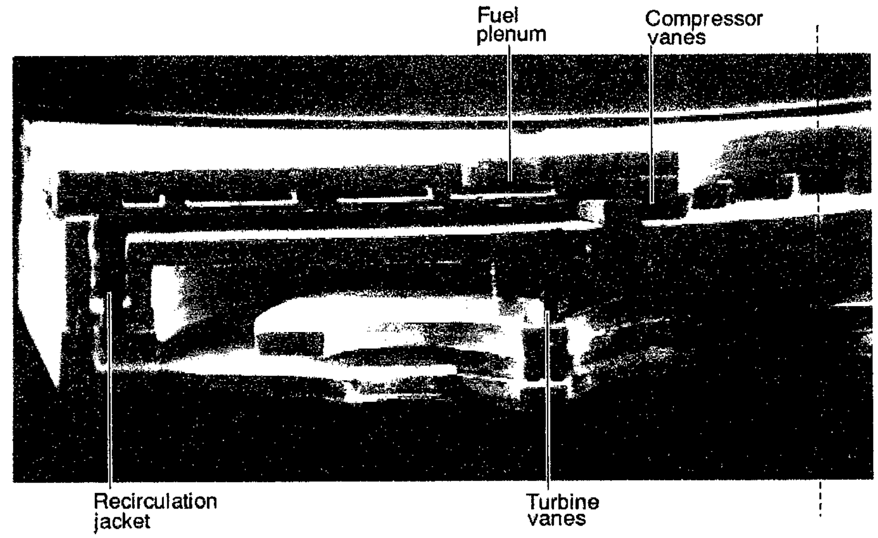
- Integrate hydrogen combustor with the other non-rotating components of the engine
- Demonstrate the ability to fabricate the completed hot flow path of a 6-wafer micro gas turbine engine
- Increase combustor efficiency within the structural constraints of silicon by designing a recirculation jacket
- Evaluate the stability boundaries for hydrogen and hydrocarbon fuels
- Validate models and analytical design tools
- Develop supporting technologies
  - Igniters
  - Fluidic / electrical interconnects
  - Temperature sensors

FEATURES OF STATIC STRUCTURE

- 12 structure masks + 4 igniter masks + 1 alignment mask
- Compatible with engine structure and fabrication sequence
- Multiple fuel injector schemes to evaluate the trade-offs between mixing and duct burning
- Fuel injectors optimized for hydrogen as well as hydrocarbon fuels
- Two types of combustor inlet holes to evaluate recirculation zone stability
- Recuperator compatible
- Compressor stator airfoils to add swirl
- Turbine NGV's to choke the flow
- Designed with "on-chip" igniters and temperature sensors

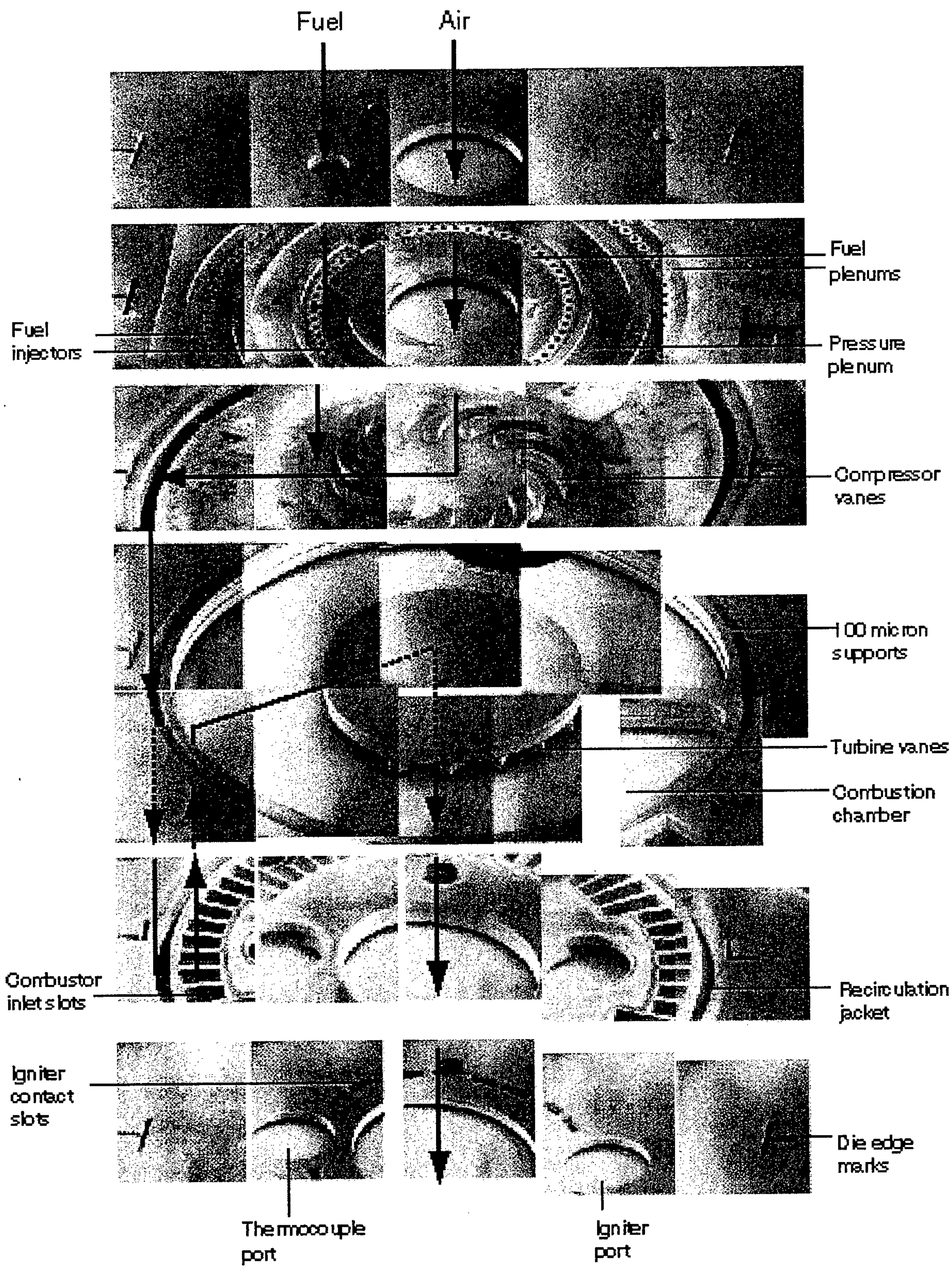
6-WAFER STATIC STRUCTURE



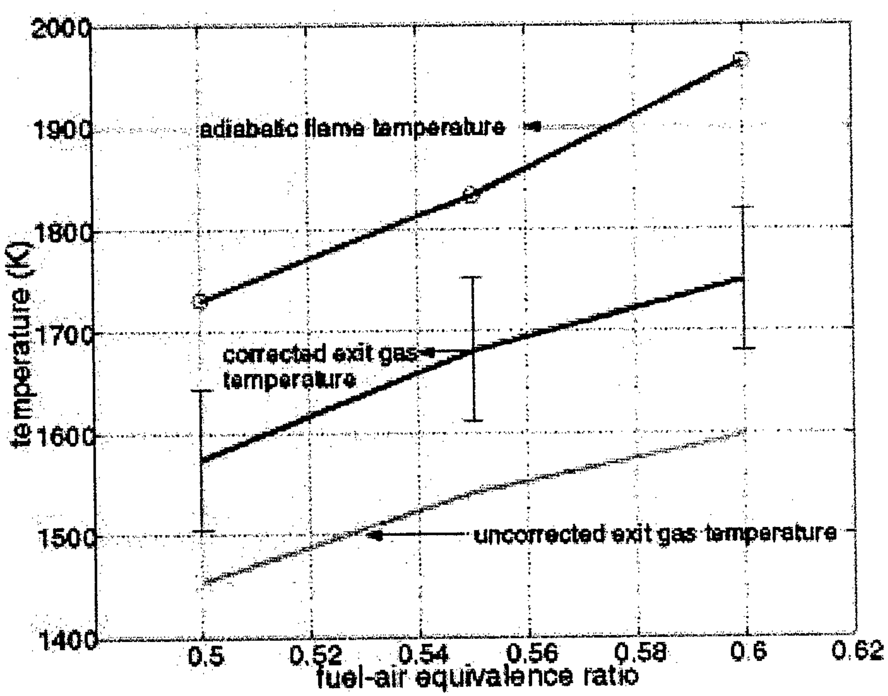


15 masks, 12 deep etches through 3.8 mm, 5 aligned wafer bonds

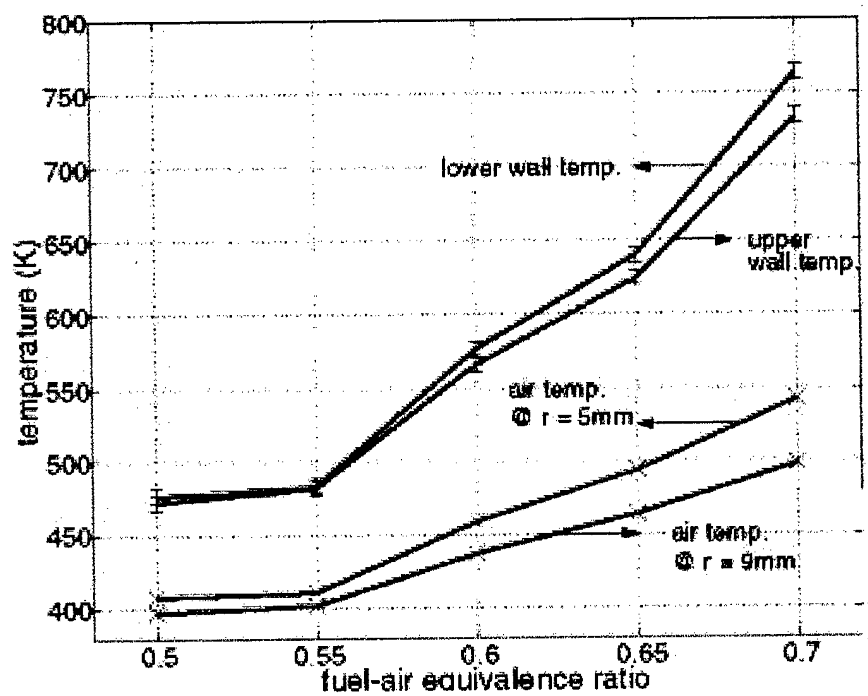
STATIC STRUCTURE



TEST RESULTS



Measured Exit Temperatures



Wall Temperatures

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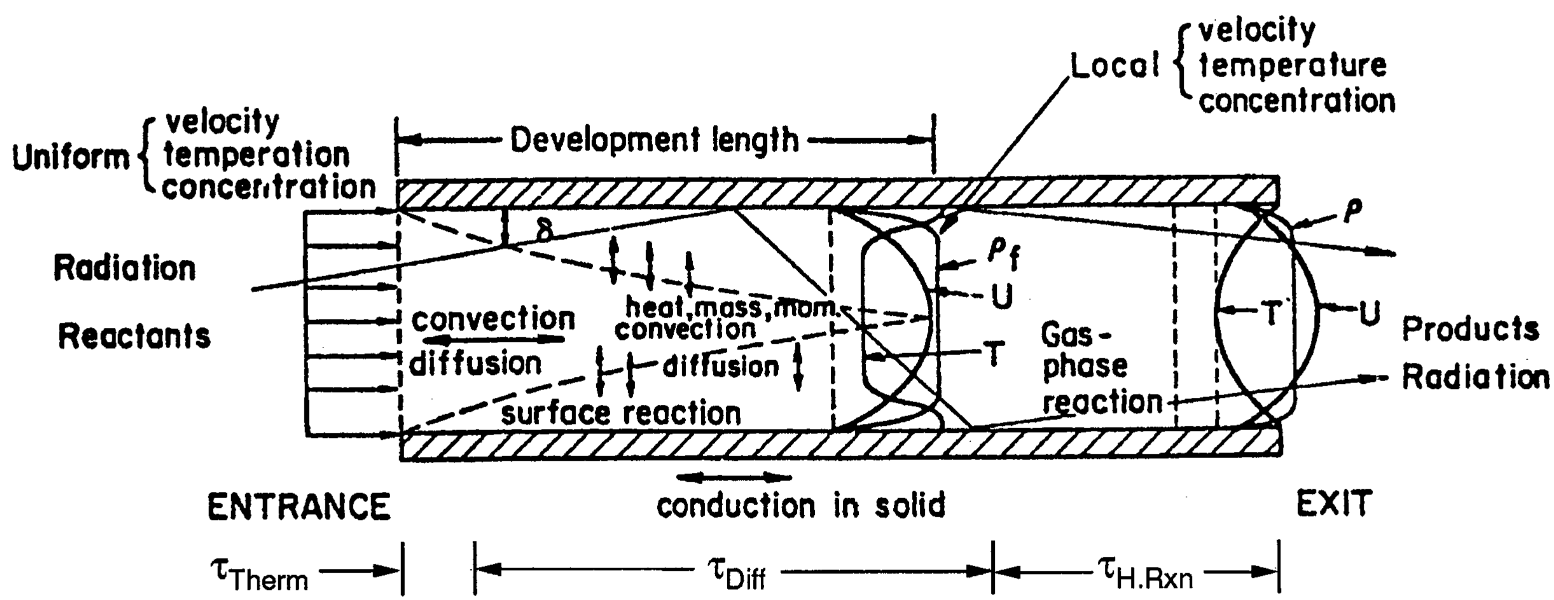
CATALYTIC COMBUSTION: TRADITIONAL PICTURE

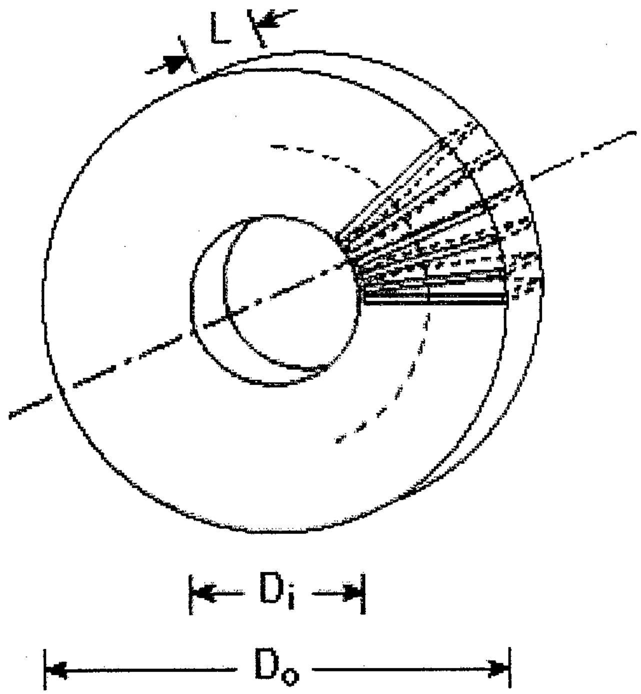


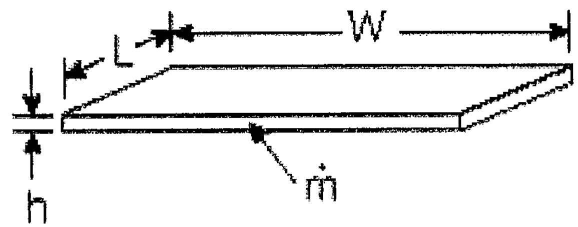
[Bracco, Bruno, Yaw, and Walsh, *Proc. Fourth Workshop on Catalytic Combustion*, Cincinnati OH, 1980]

Three regions governed respectively by:

1) **Heat transfer**
2) **Mass transfer**
3) **Homogeneous Reaction**

CATALYTIC COMBUSTION
– 1st Order Model –





- Diffusion limited
- Fast chemistry

Complete combustion:

$$\tau_{conv} = \tau_{diff}$$

$$\frac{L}{u_{conv}} = \frac{h^2}{2D_{AB}\ln(1-x_A)}$$

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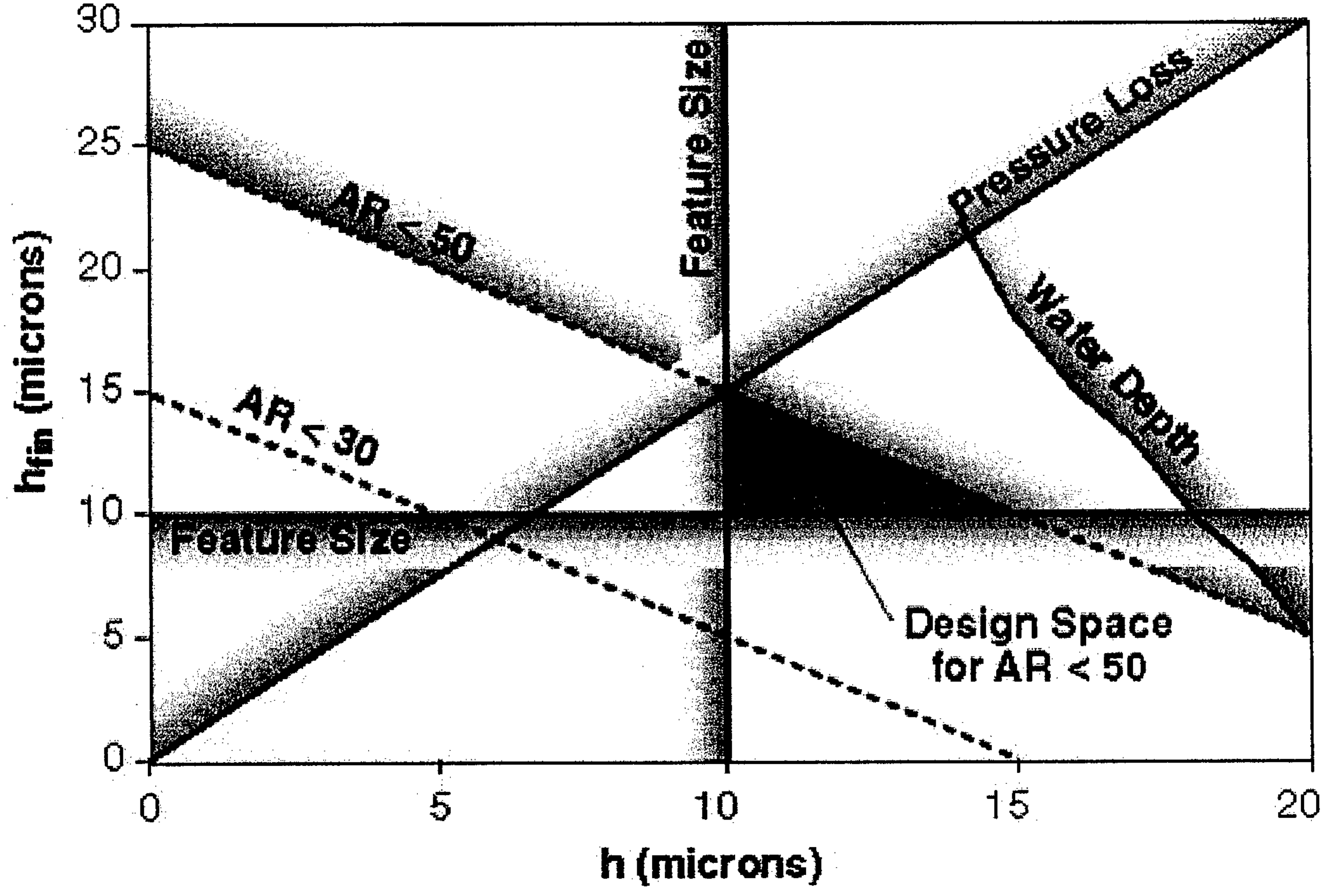
DESIGN SPACE FOR CATALYTIC COMBUSTOR

(T = 1025 K, $X_{C_3H_8} = 0.03$, $\phi = 0.95$)



IMPLICATIONS FOR CATALYTIC COMBUSTION

- High temperature materials (e.g. SiC) are required
- Feasible design space exists
  - Given constraints on pressure loss, fabrication, geometry, diffusion speed
- Hybrid Si/SiC catalytic combustor under development

COMBUSTOR DEVELOPMENT SUMMARY

- Defined design space for hydrogen and catalytic-hydrocarbon combustion
- Demonstrated working hydrogen combustor with power density one order of magnitude higher than existing power-MEMS
  - Satisfies all functional requirements and constraints for first micro gas turbine demo engine
  - Establishes the viability of silicon for these applications
- 6-wafer static structure - integrated combustor with all non-rotating components of engine (ignitors, packaging, etc.)
  - Demonstrated wafer-level fabrication procedure for demo-engine (deep etching, aligned fusion bonding, die-sawing, interconnects, etc.)
  - Will serve as primary test bed for determining hydrogen and hydrocarbon stability boundaries, fuel injector configurations, thermal design issues
- Parallel catalytic development efforts on-going

KEY ISSUES AND NEEDS
- Combustors for Micro Heat Engines -

- Power density and microfabrication requirements are key drivers
  - High temperature material fabrication processes
  - Diagnostics compatible with micro devices
  - Catalytic/hydrocarbon modeling and simulation
  - Fuel delivery/throttling/vaporization systems
  - Thermal management
  - Novel ideas
- Successful devices will only result from rigorous multi-disciplinary engineering

CONCLUSIONS

- MEMS-based thermal engines appear
  - Possible
  - Promising
  - Useful
- An MIT team is well underway to produce MEMS-based
  - Turbine generators
  - Motor-driven compressors
  - Gas turbines
  - Rocket engines

MANPORTABLE MICROTECHNOLOGY-BASED ABSORPTION HEAT PUMP

Michele Friedrich, M. Kevin Drost
Peter Armstrong, Jim Bates,
Nathan Bauman, Kriston Brooks,
Daryl Brown, Rick Cameron,
Bill Hanna, Darrel Hatley

P.O. Box 999
Richland, WA 99532

U.S. Department of Energy
Pacific Northwest National Laboratory

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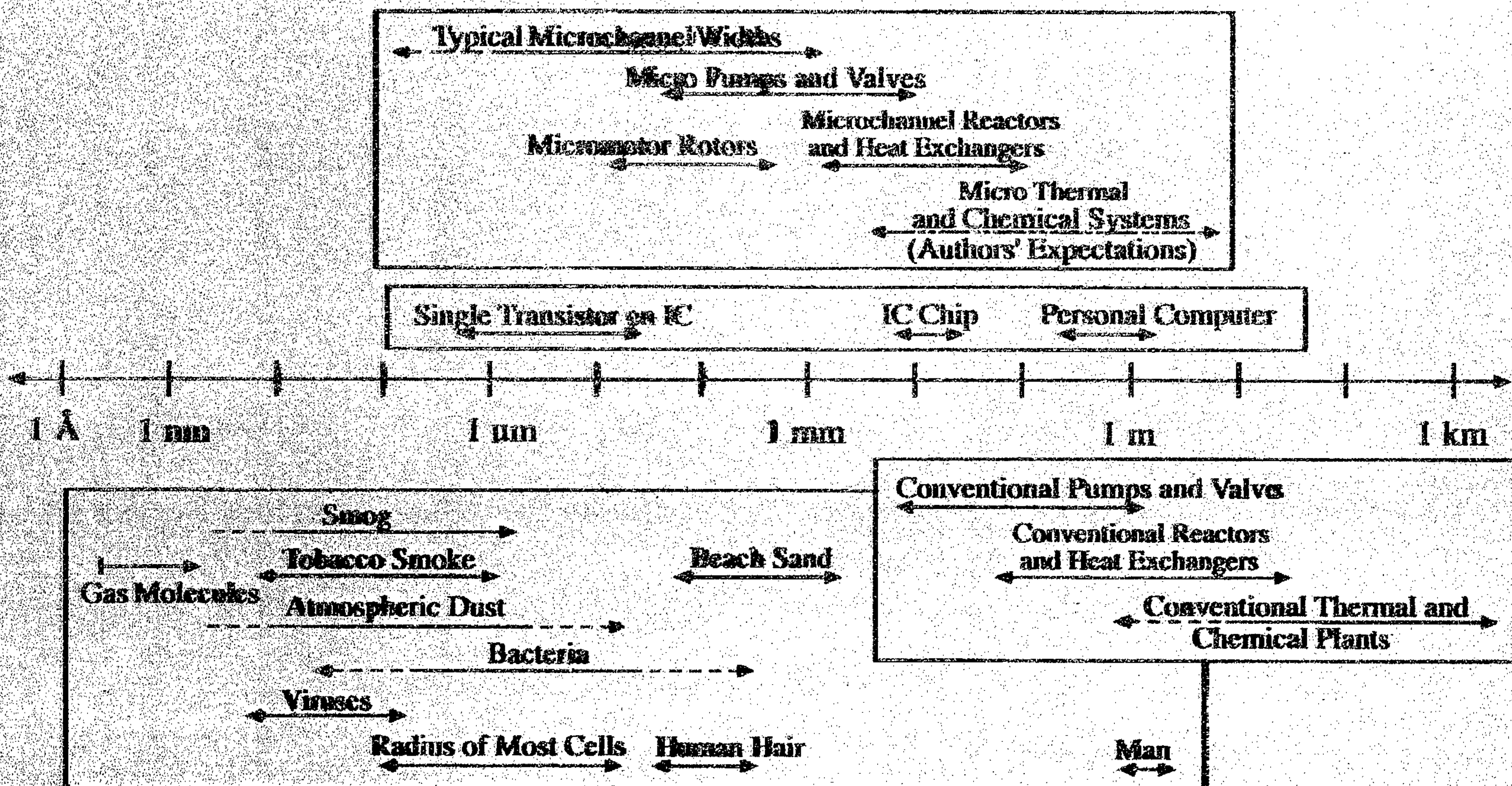
WHY MINITURIZE ENERGY AND CHEMICAL SYSTEMS?



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ABSORPTION HEAT PUMP CONCEPT DESCRIPTION

The absorption and vapor-compression cycles differ in the way compression is provided, however, both systems take the same approach to heat absorption and rejection.

Compression is accomplished in the absorption heat pump with a single-effect thermochemical compressor consisting of an absorber, a solution pump, a desorber, and a regenerative heat exchanger.

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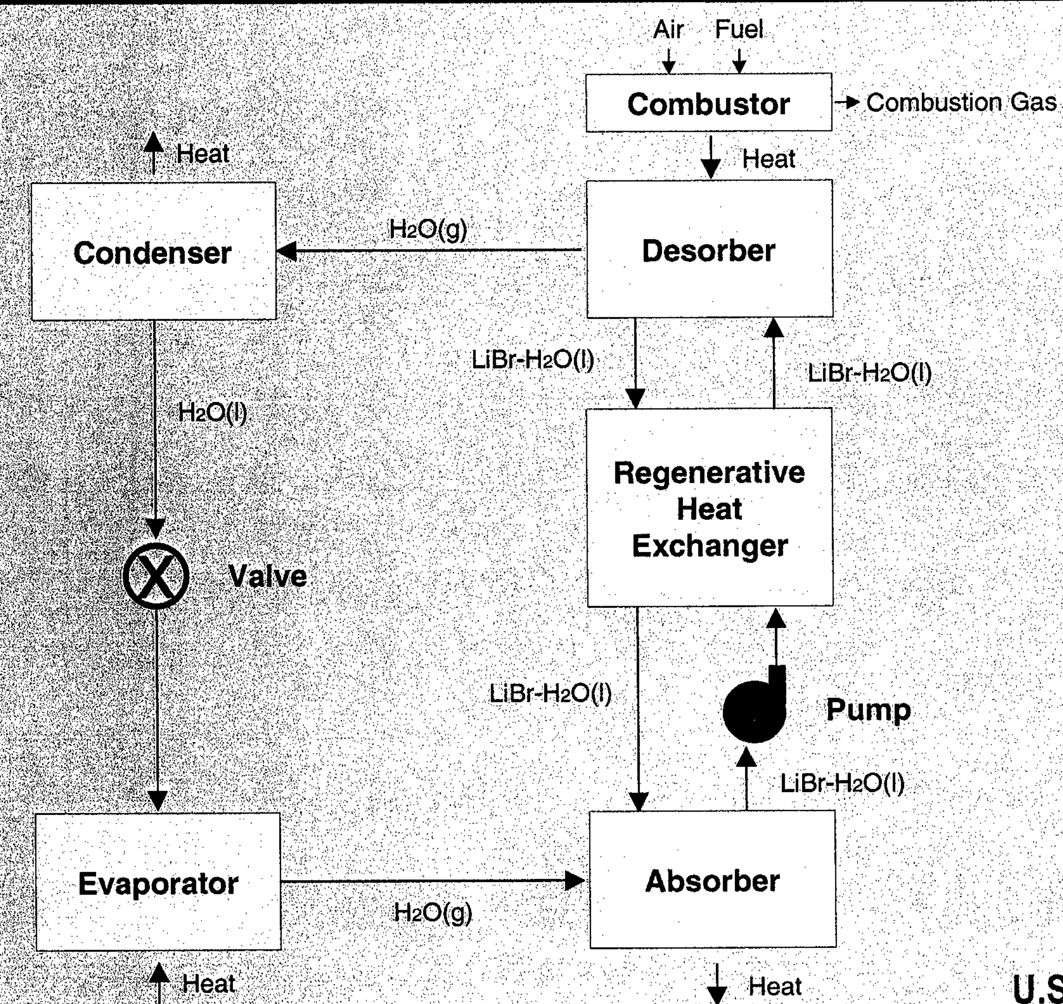
SINGLE-EFFECT ABSORPTION HEAT PUMP



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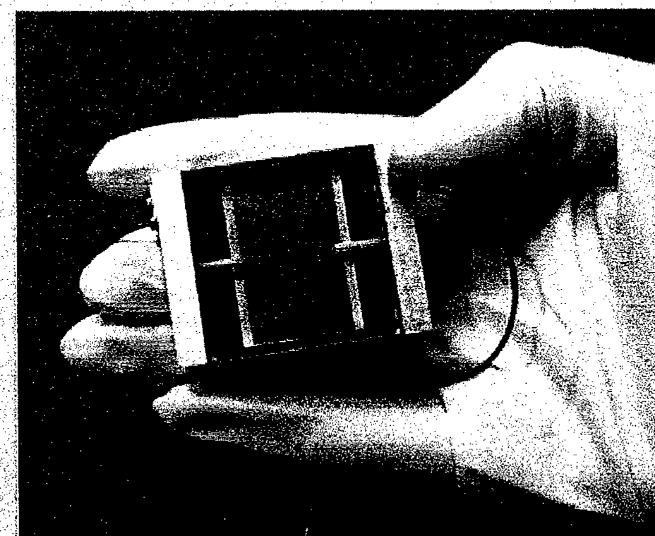
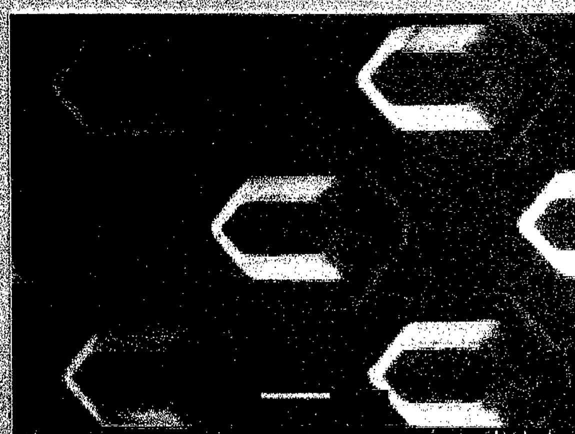
MICROCHANNEL HEAT EXCHANGERS

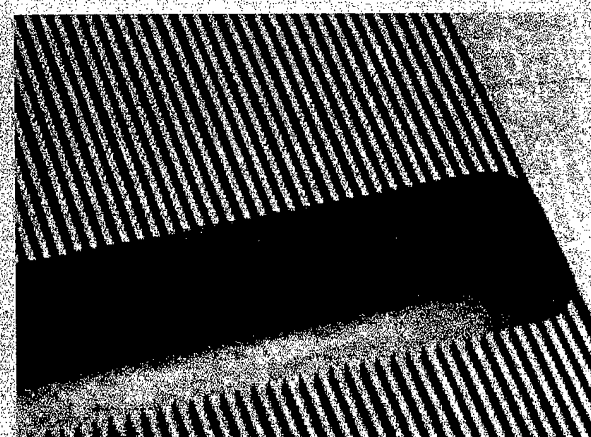
- Heat fluxes: 100^{+} watts/cm^2
- Low pressure drops: 1-2 psi
- High convective heat transfer coefficients:

  Single phase: 1-1.5 W/cm^2-K

  Phase change: 3-3.5 W/cm^2-K







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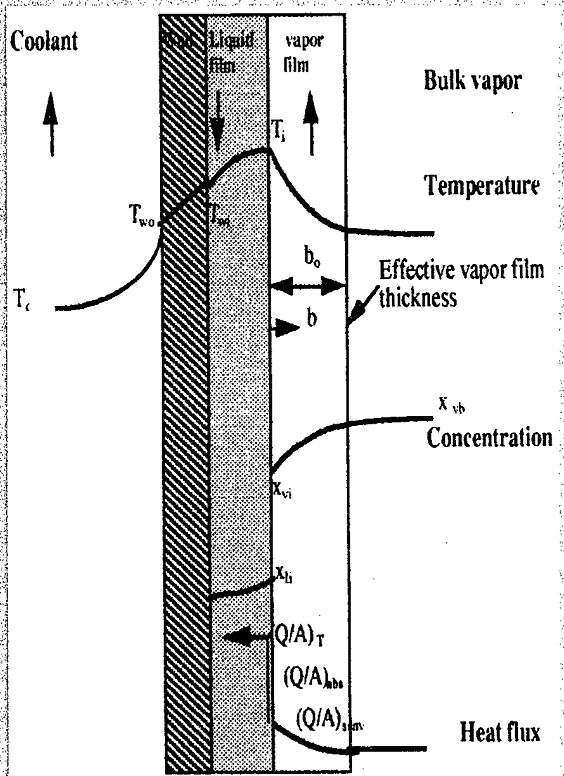
ABSORPTION AND DESORPTION

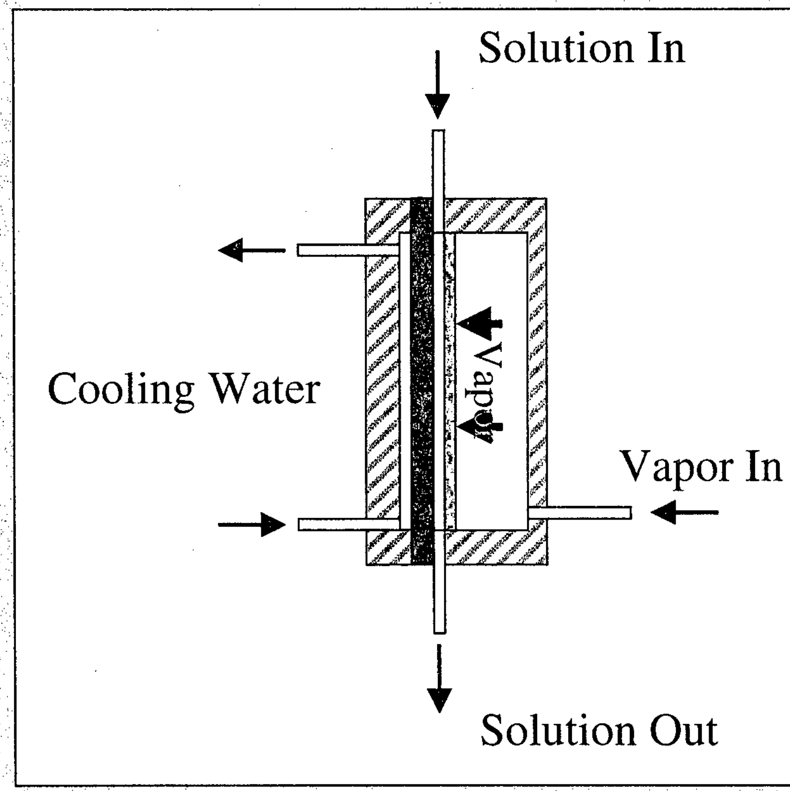
A conventional absorption heat pump relies on gravity to form falling films.

Falling films have a film thickness on the order of 1 mm which is a significant barrier to mass diffusion.

ABSORBER



Gravity Falling Film



Constrained Thin Film

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ABSORPTION AND DESORPTION

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The reduction in the thickness of the thin film from 200 microns to 50 microns would reduce the length by a factor of 16 while keeping the sorption rate constant.

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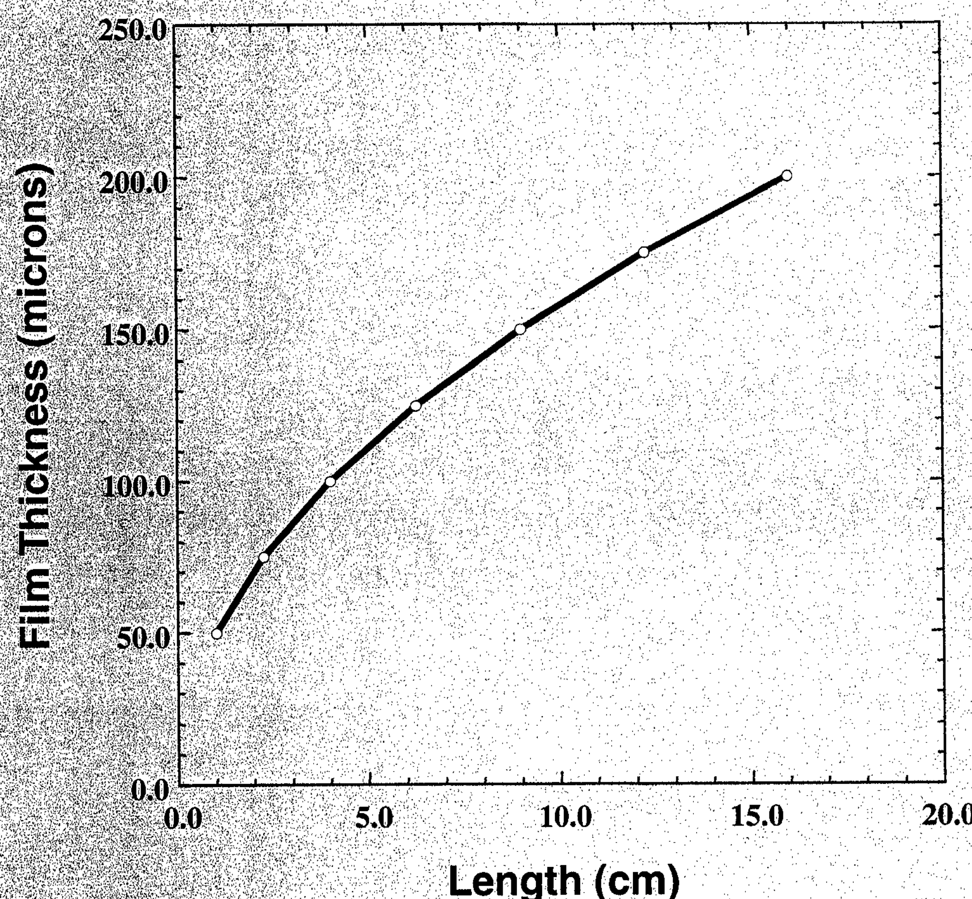

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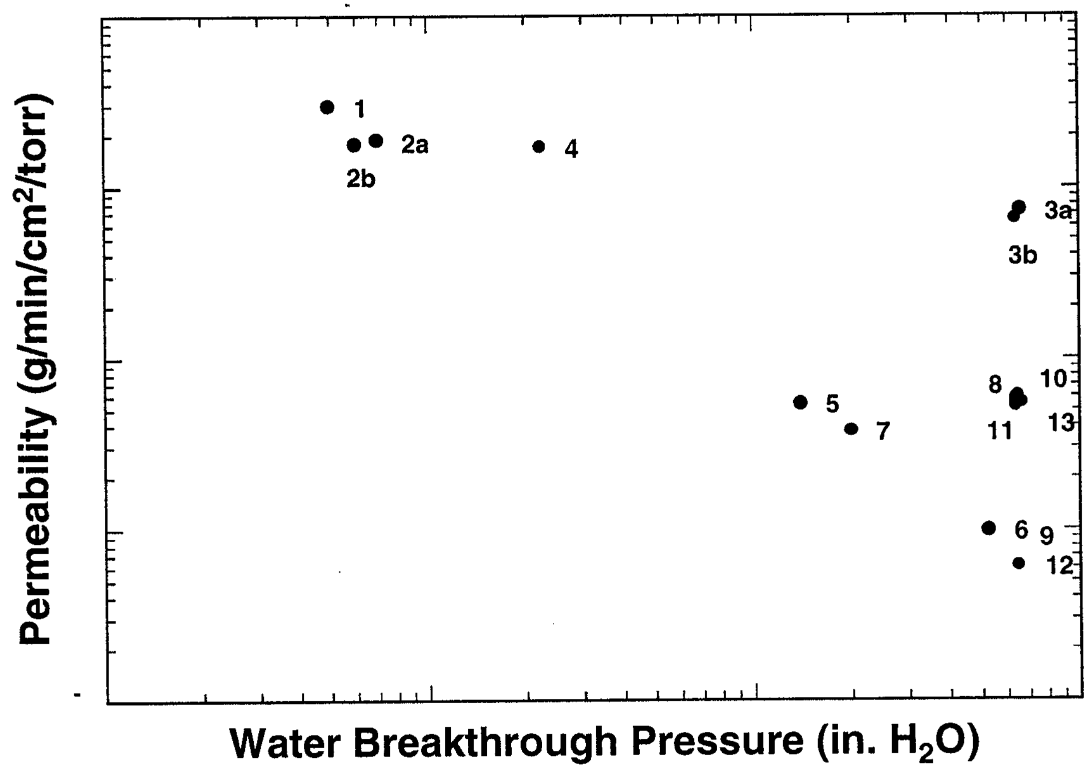
CONTACTORS

The desorber and absorber depend on the micromachined contactors to prevent liquids from passing though the contactor while minimizing impact of water vapor diffusion.

CONTACTORS



Permeability versus supported liquid pressure

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RELATED PREVIOUS WORK: COMPONENT PERFORMANCE TEST DATA

- Evaporator U value: 3600 to 7400 W/m^2-K (200-420% of conventional)
- Absorber U value: 3300 to 5500 W/m^2-K (220-380% of conventional)
- Absorber mass transfer rate: 44.5 to 133 kg/m^2-hr (540-1600% of conventional)
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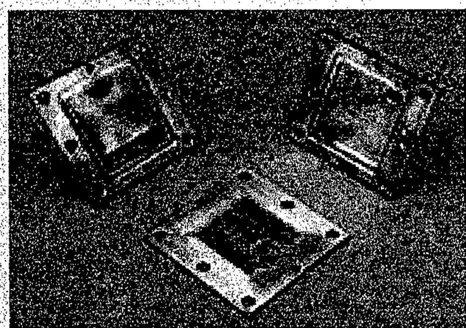
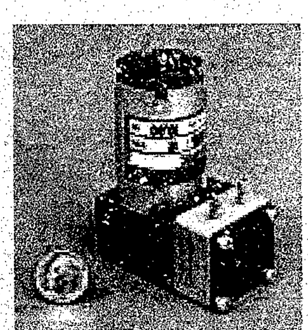
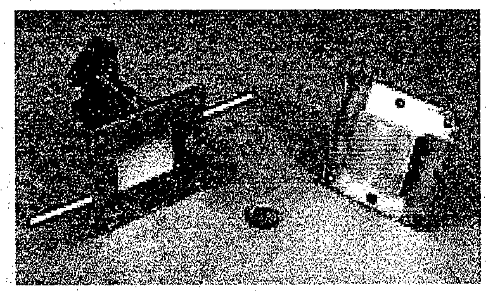
MICROTECHNOLOGY-BASED BENCHTOP LiBr ABSORPTION HP



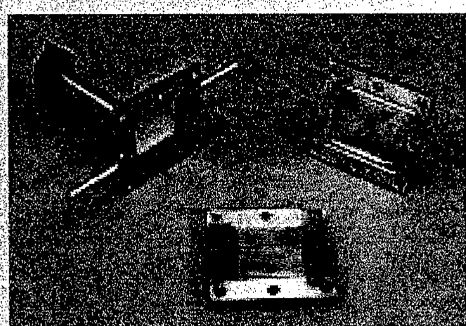
Evaporator



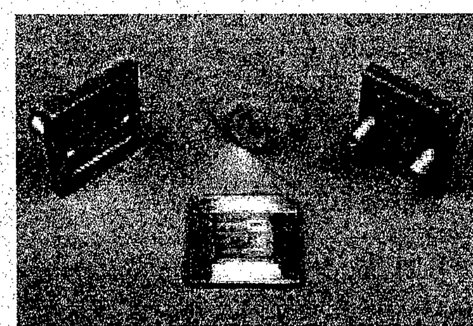
Pump



Desorber



Absorber



Regenerative Heat Exchanger

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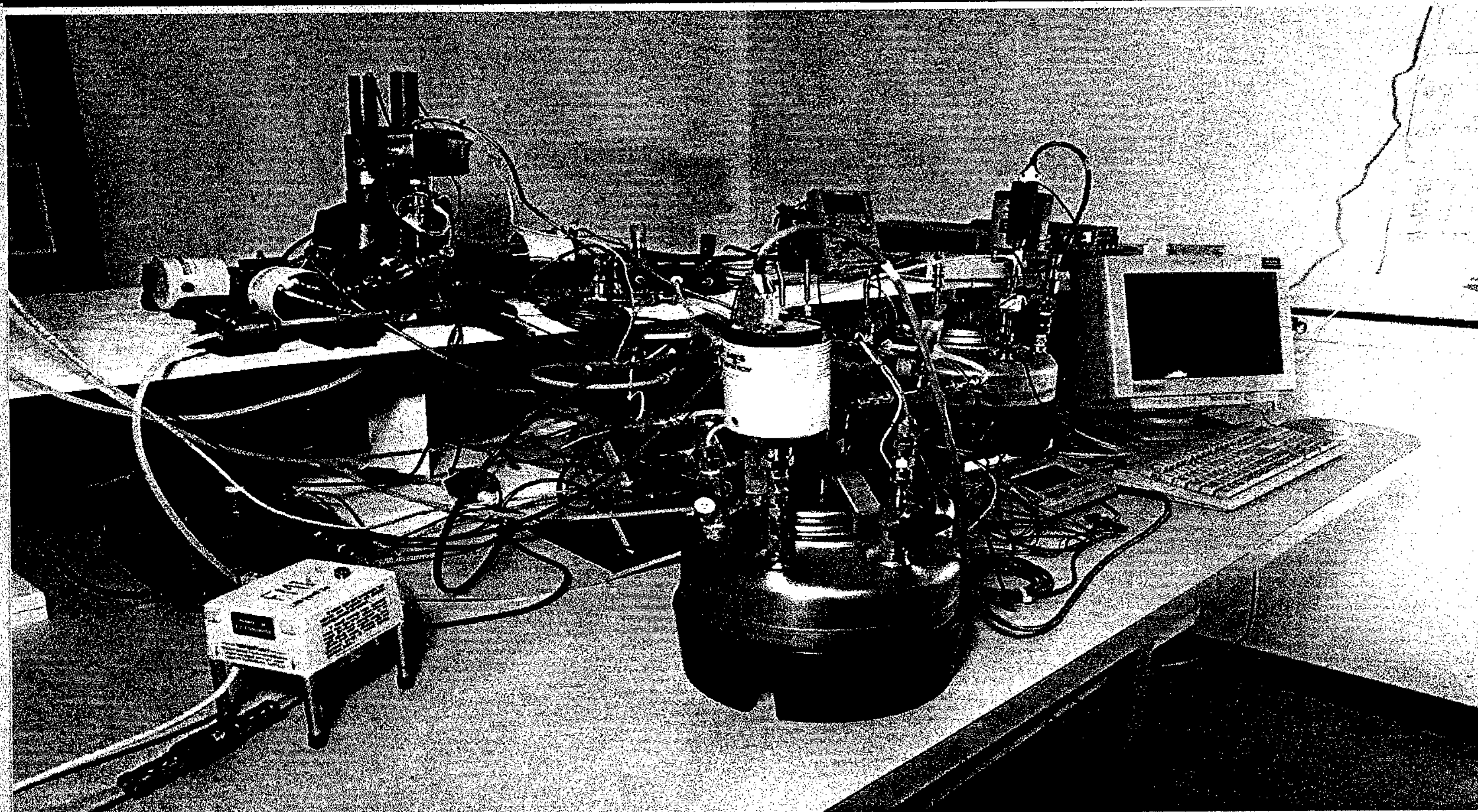
MICROTECHNOLOGY-BASED HP BENCHTOP TEST LOOP



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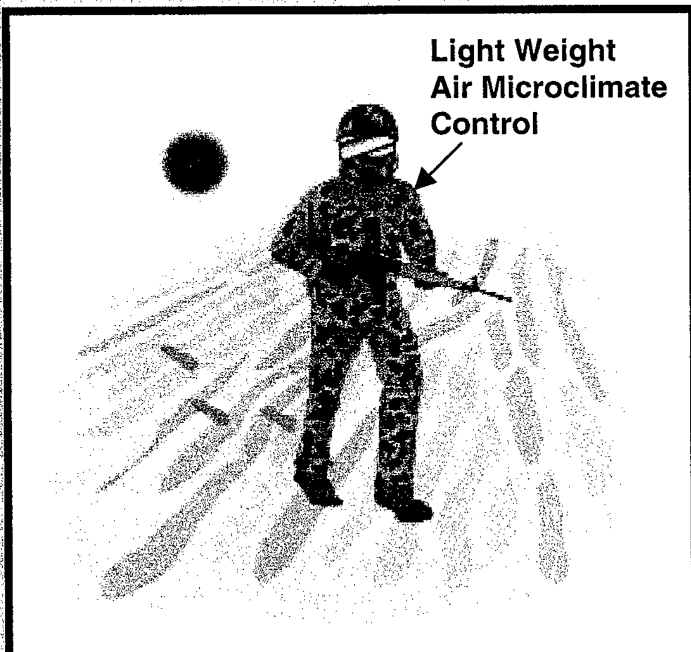
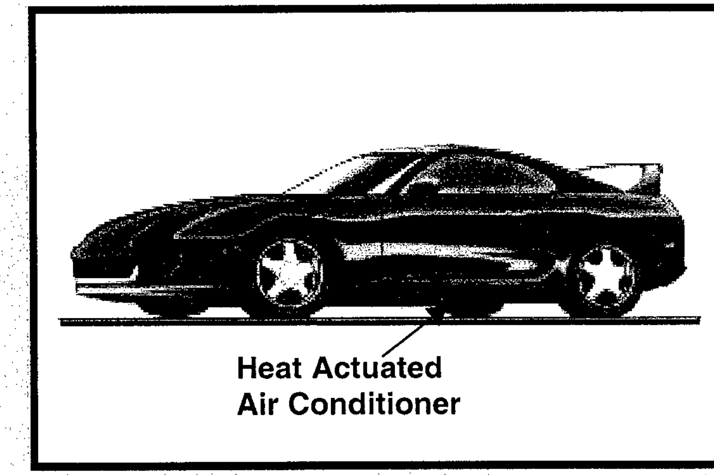
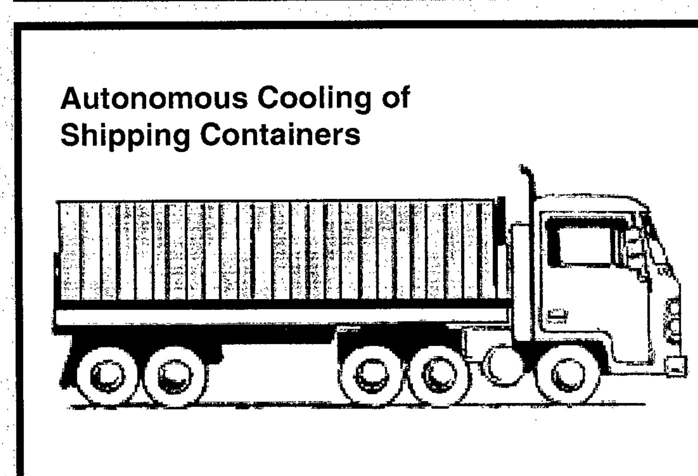
MICROTECHNOLOGY-BASED HEAT PUMP - APPLICATIONS







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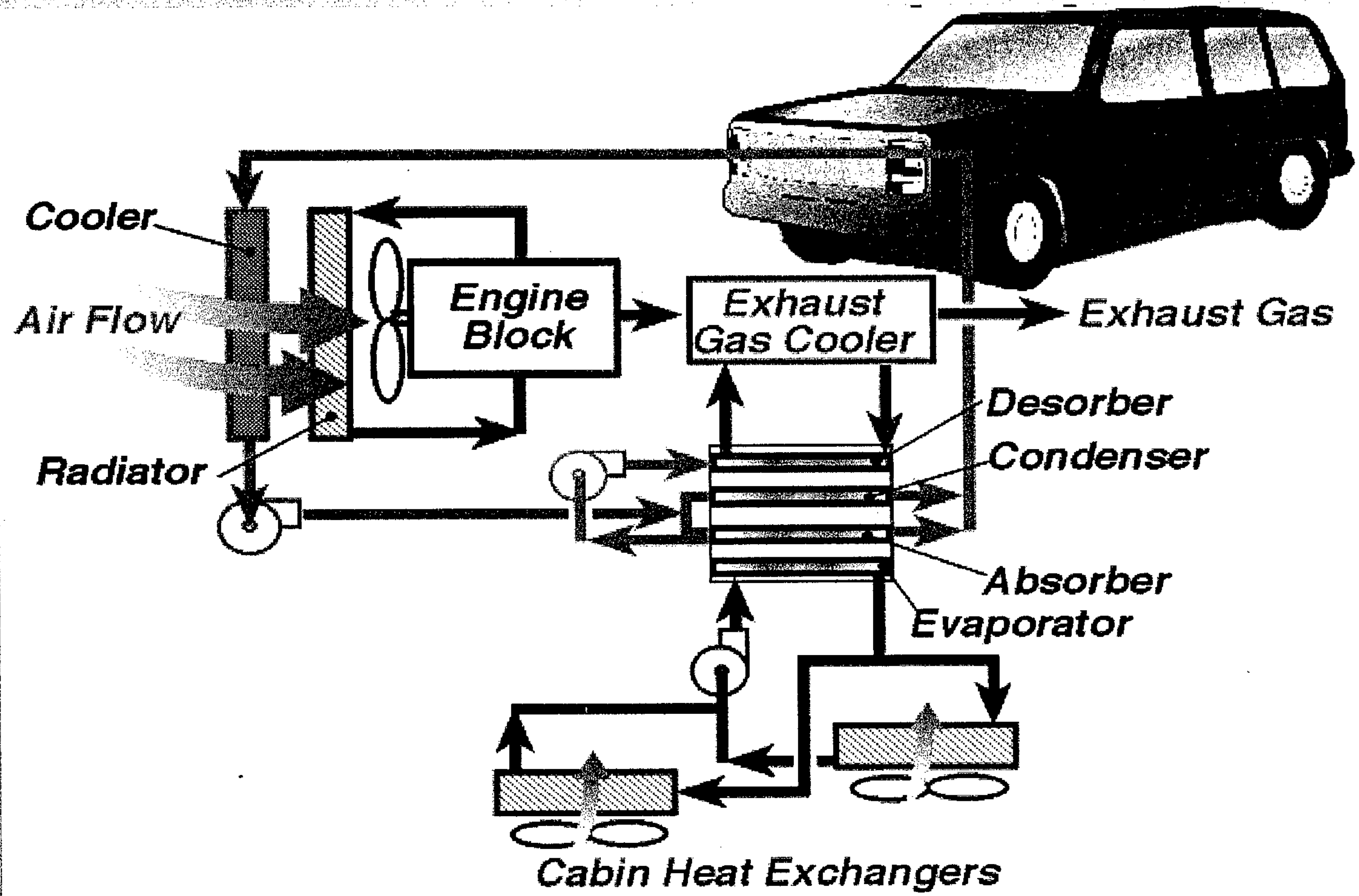
MICROTECHNOLOGY-BASED HEAT PUMP : AUTOMOBILES



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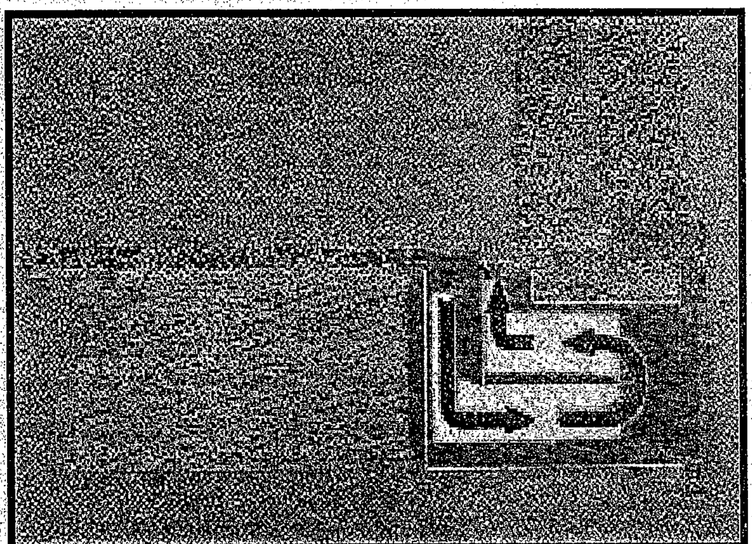
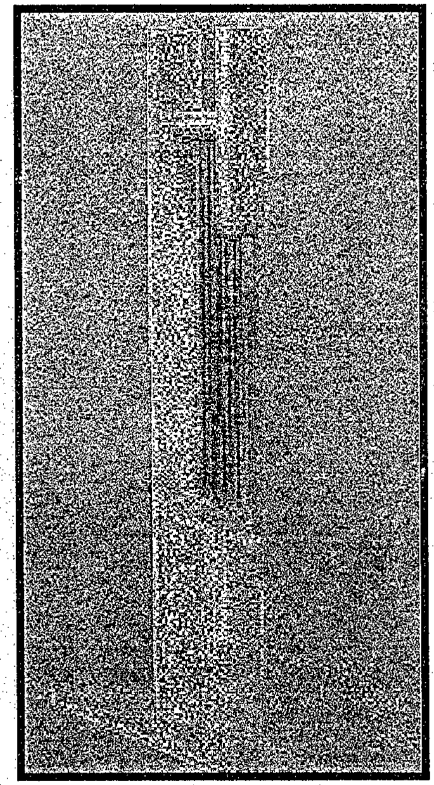
MICROTECHNOLOGY-BASED HEAT PUMP : BUILDINGS



In-Joists



In-Wall

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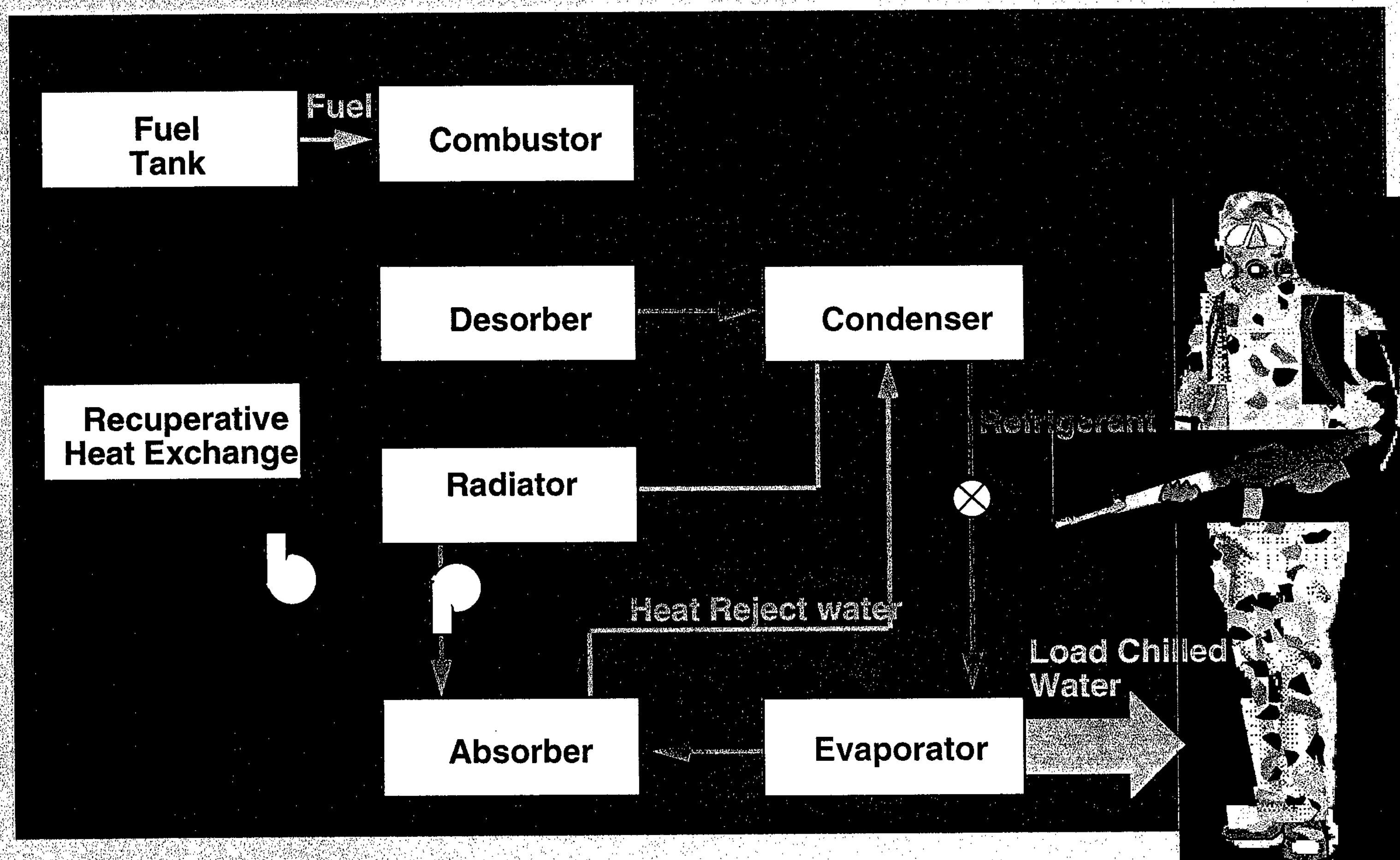
DARPA PROGRAM
MANPORTABLE ABSORPTION CHILLER



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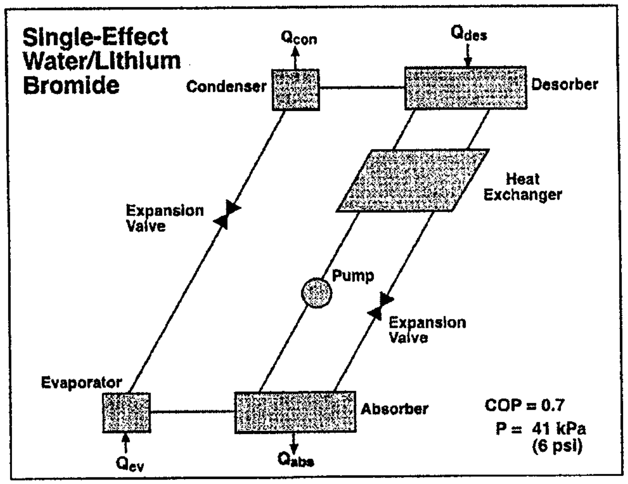
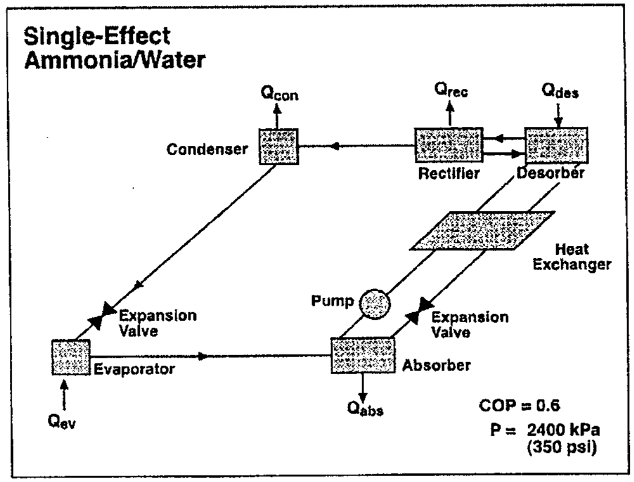
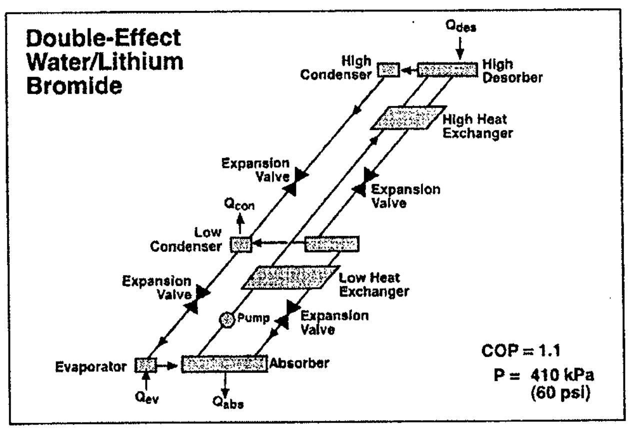
KEY DESIGN DECISION - WHAT ABSORPTION CYCLE?







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KEY DESIGN DECISION - WHAT ABSORPTION CYCLE?

Component	H2O-LiBr SEC	NH3-H2O SEC	H2O-LiBr DEC
	kg	kg	kg
RADIATOR	1.2	1.3	1.0
HYDRONIC PUMPS	0.3	0.3	0.3
FAN	0.1	0.1	0.1
MOTOR	0.2	0.4	0.3
FUEL & TANK	0.5	0.6	0.4
COMBUSTOR	0.1	0.1	0.1
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SOLUTION PUMP	0.2	7.3	0.2
BATTERY	1.1	1.9	1.1
STRUCTURE	0.9	1.0	0.8
TOTAL	5.0	13.5	5.4

MANPORTABLE HEAT PUMP PERFORMANCE

Based on experimental data we have collected, a prototype single-effect LiBr/H_2O, manportable, 350 W cooler has been designed.

One system uses a battery to provide electric power for pumps and the fan, while the second system uses a thermoelectric generator (TEG) installed between the combustor and the desorber to provide electric power.

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	Power Source	
Component	NiCd BATTERY	PbTe TEG
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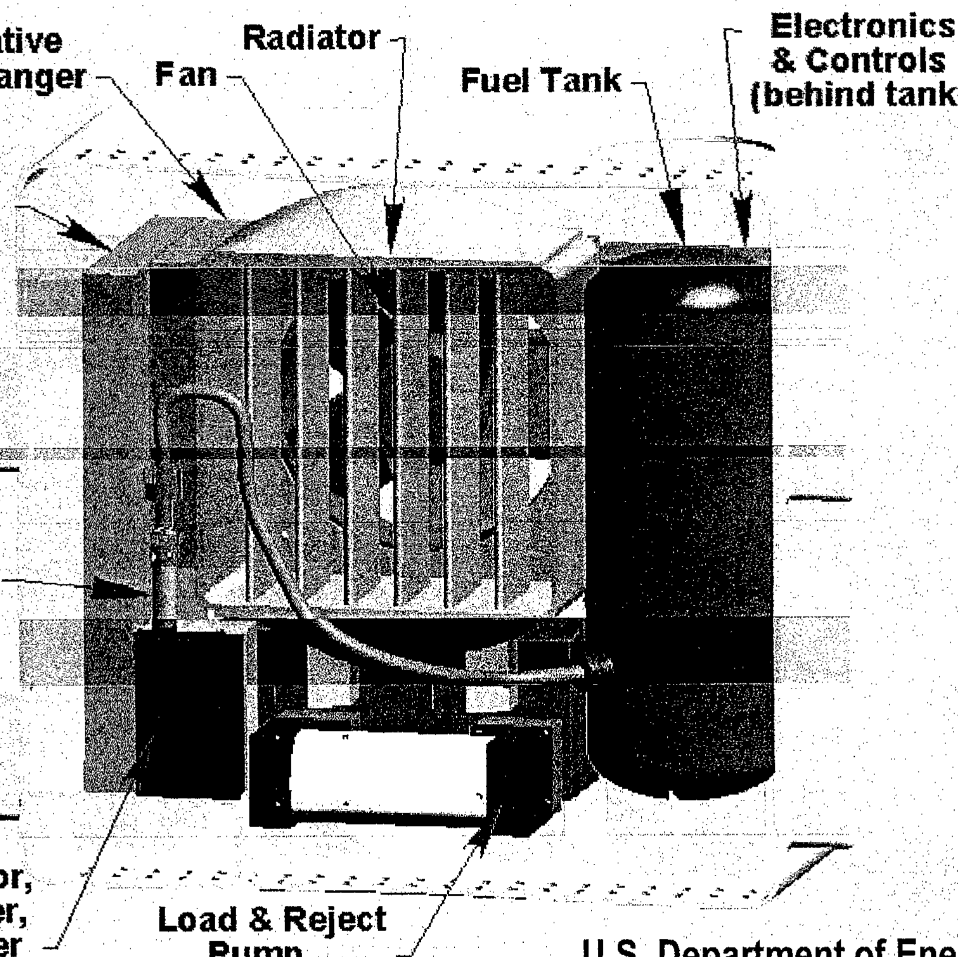
TOTAL	5.14	4.67

DARPA MANPORTABLE COOLER

5.1 kg

350 W cooling for 8 hours



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CONCLUSIONS

By taking advantage of the high rates of heat and mass transfer attainable in microstructures, PNNL is developing a miniature absorption heat pump with a cooling capacity of 350 W that weighs only 1 kg and is less than 600 cm^3. Compared to a conventional absorption heat pump, this is a reduction in volume by a factor of 60.

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CONCLUSIONS

A complete manportable cooling system, including the heat pump, an air-cooled heat exchanger, batteries, and fuel, is estimated to weigh between 4 and 5 kg, compared to the 10-kg weight of alternative systems.

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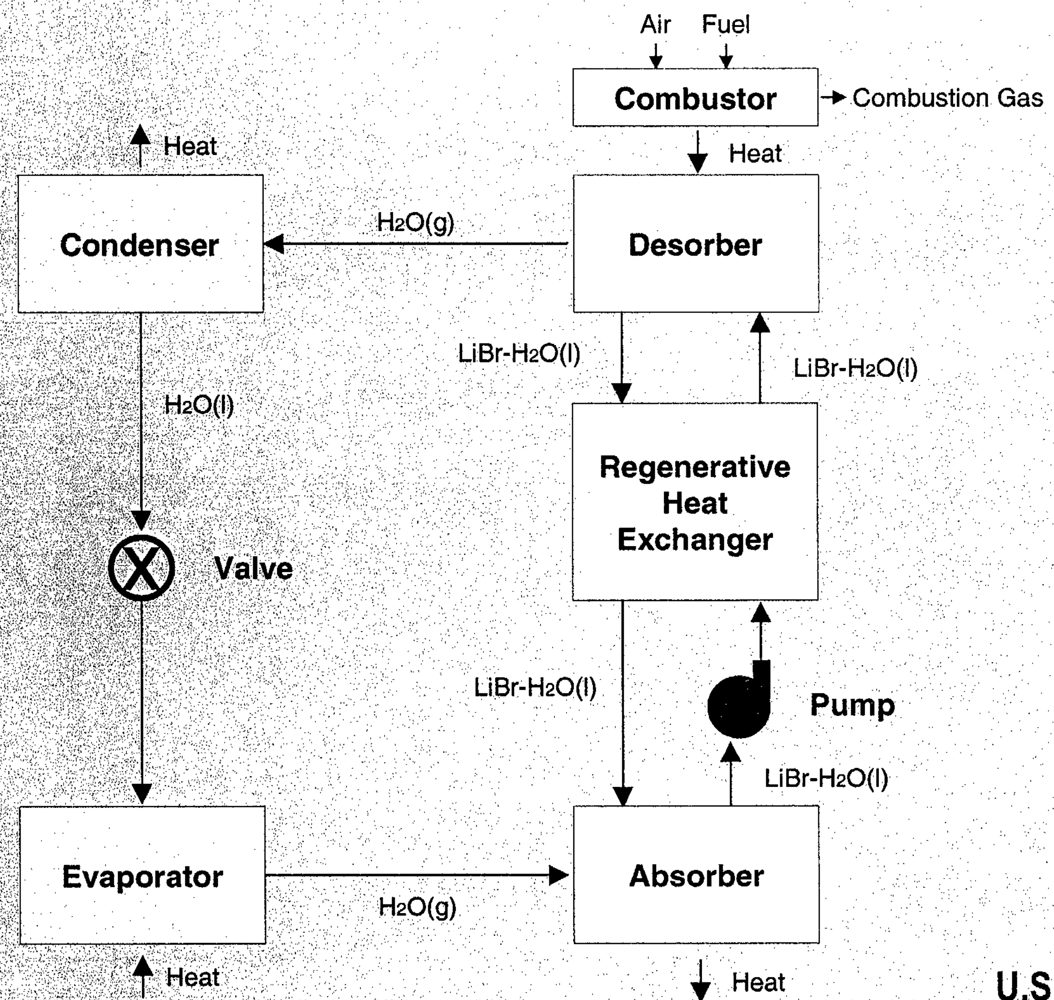
ABSORPTION HEAT PUMP CONCEPT DESCRIPTION

The absorption and vapor-compression cycles differ in the way compression is provided, however, both systems take the same approach to heat absorption and rejection.

Compression is accomplished in the absorption heat pump with a single-effect thermochemical compressor consisting of an absorber, a solution pump, a desorber, and a regenerative heat exchanger.

SINGLE-EFFECT ABSORPTION HEAT PUMP



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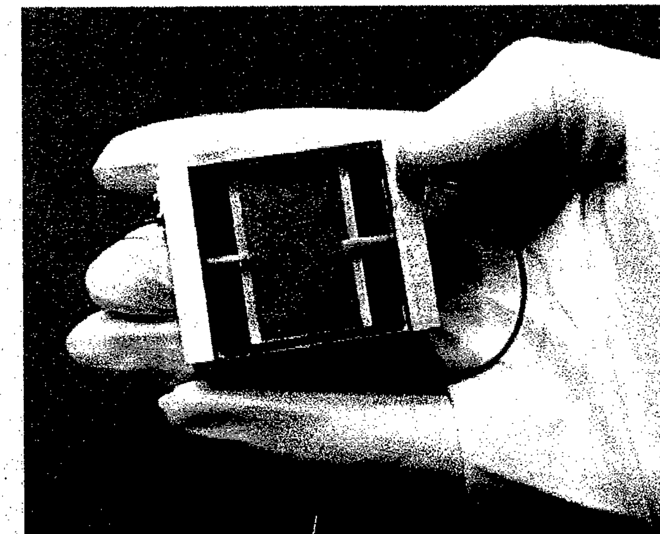
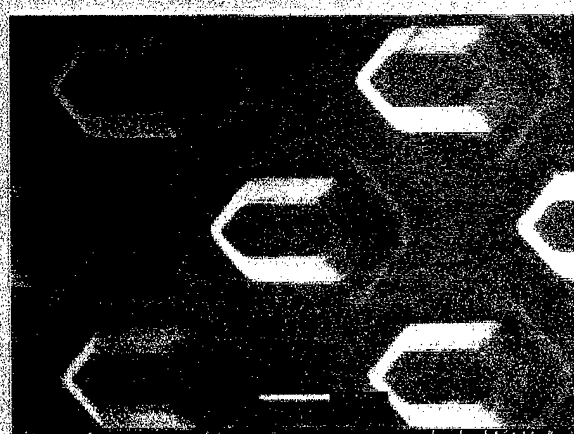
MICROCHANNEL HEAT EXCHANGERS

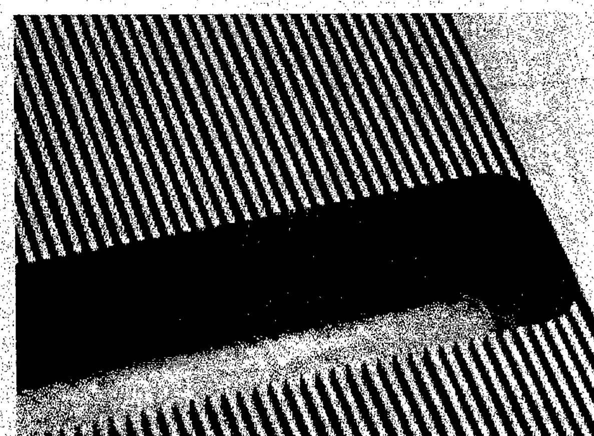
- Heat fluxes: 100^{+} watts/cm^2
- Low pressure drops: 1-2 psi
- High convective heat transfer coefficients:

  Single phase: 1-1.5 W/cm^2-K

  Phase change: 3-3.5 W/cm^2-K







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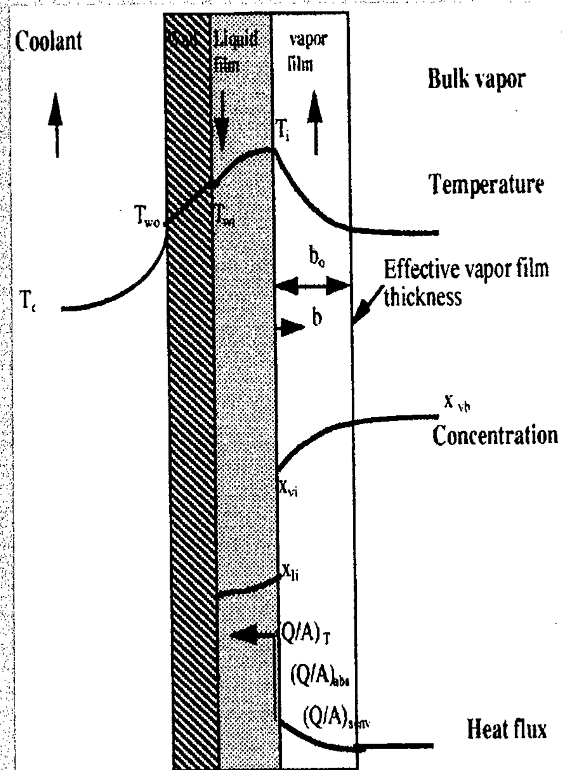
ABSORPTION AND DESORPTION

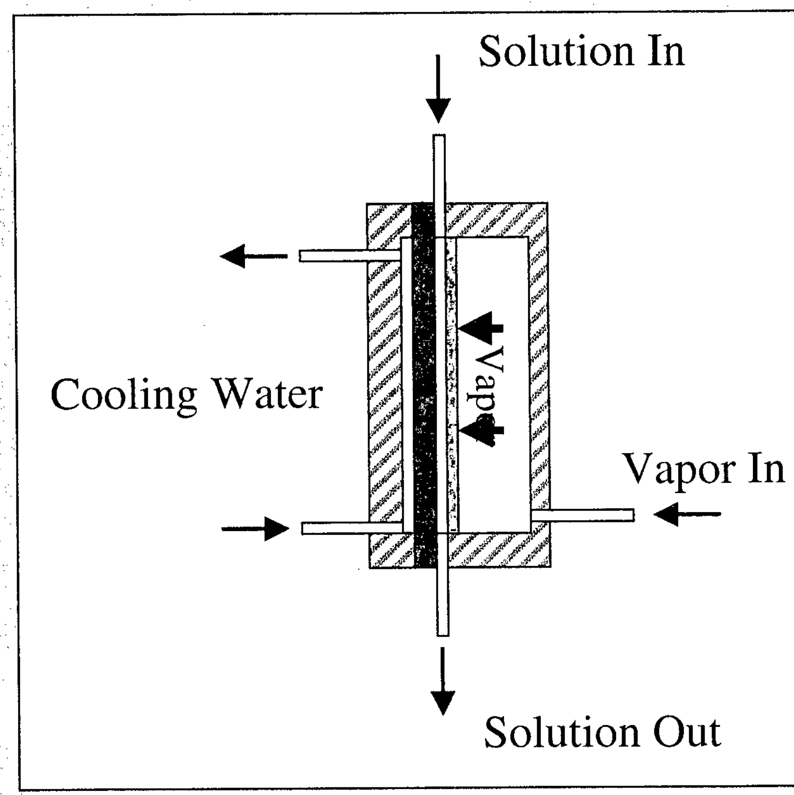
A conventional absorption heat pump relies on gravity to form falling films.

Falling films have a film thickness on the order of 1 mm which is a significant barrier to mass diffusion.

ABSORBER



Gravity Falling Film



Constrained Thin Film

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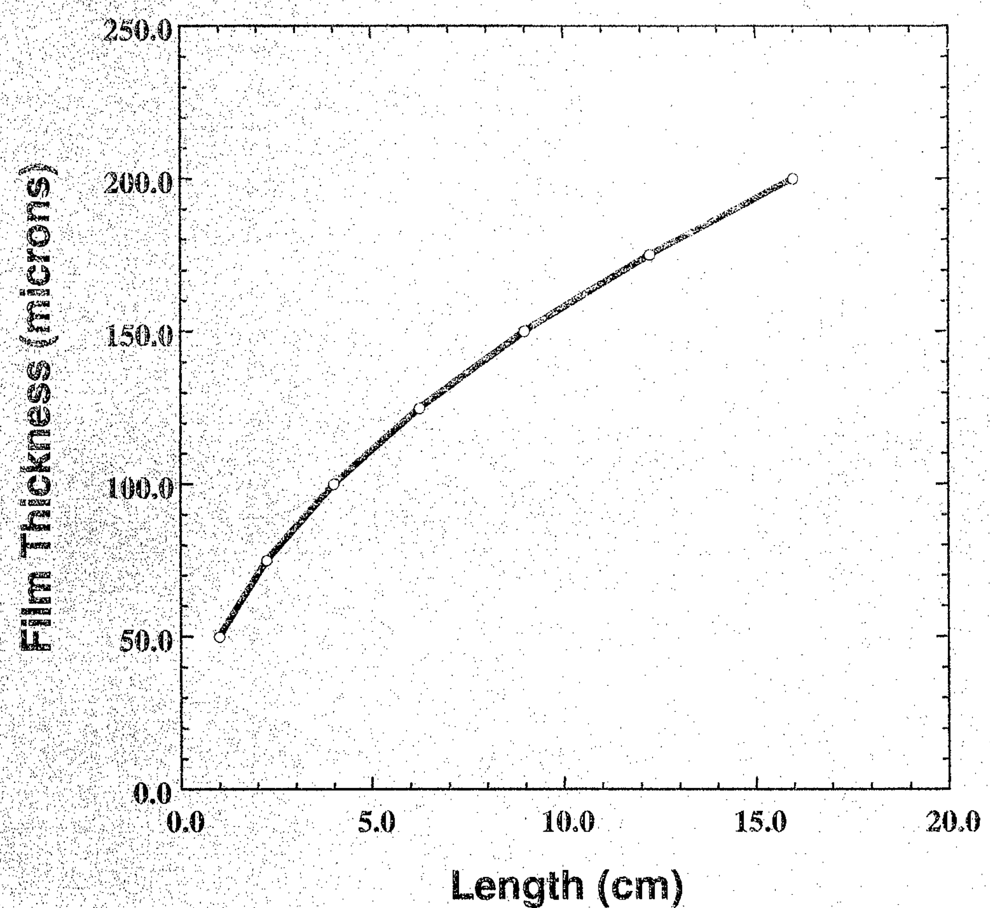

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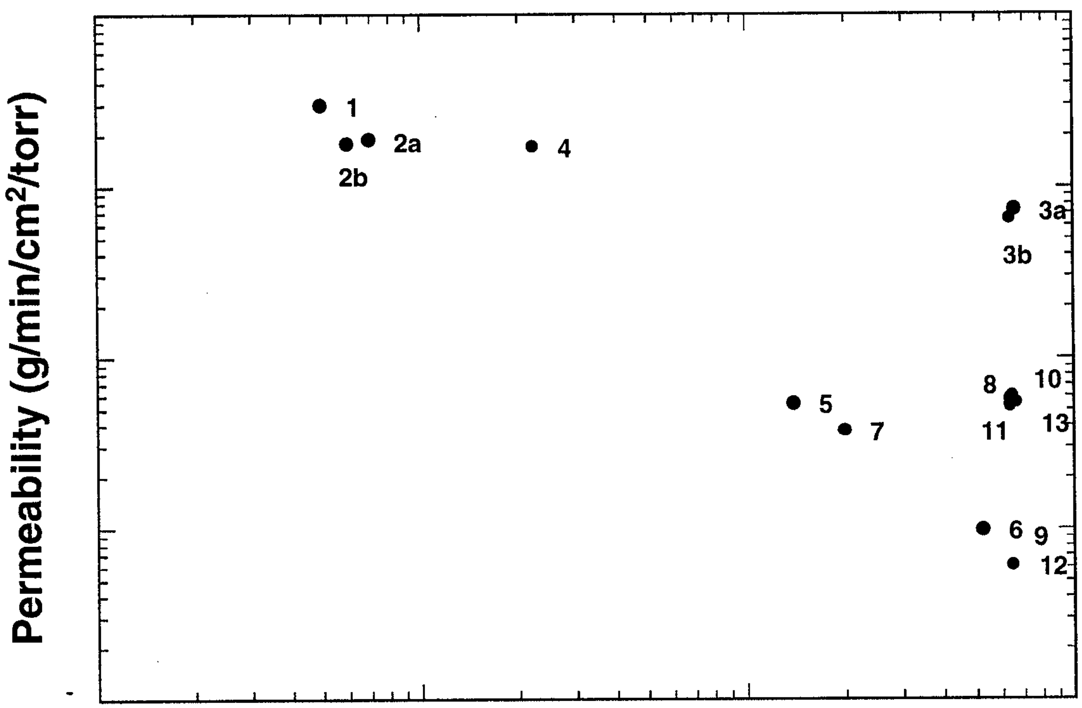

Permeability versus supported liquid pressure

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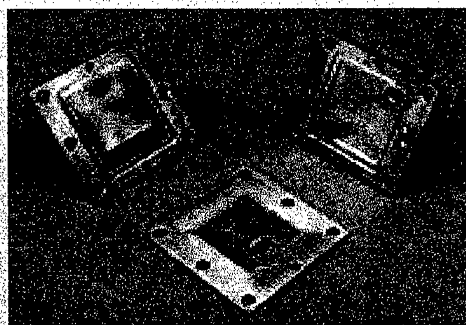
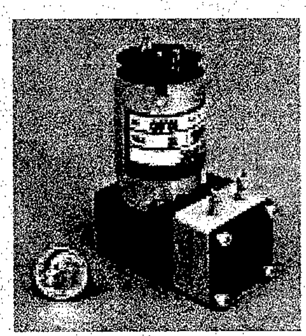
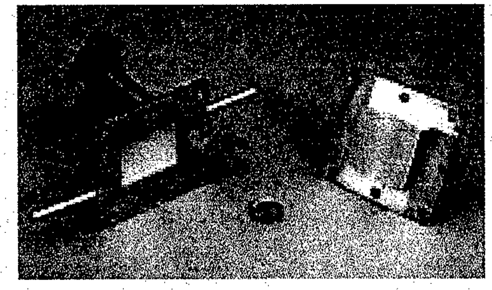
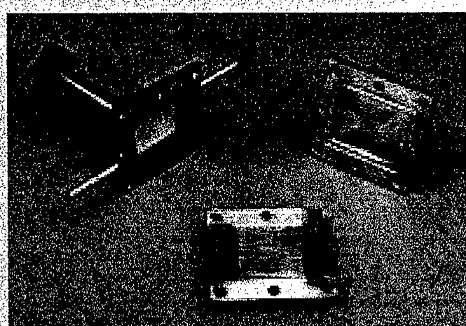
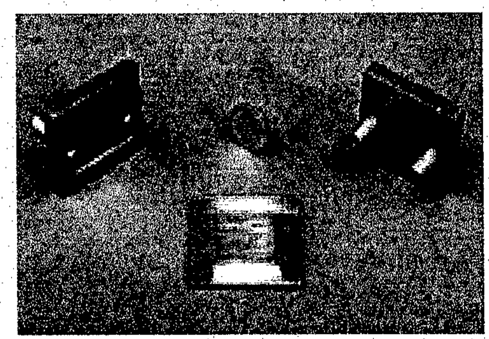
MICROTECHNOLOGY-BASED BENCHTOP LiBr ABSORPTION HP


Evaporator


Pump


Desorber


Absorber


Regenerative Heat Exchanger

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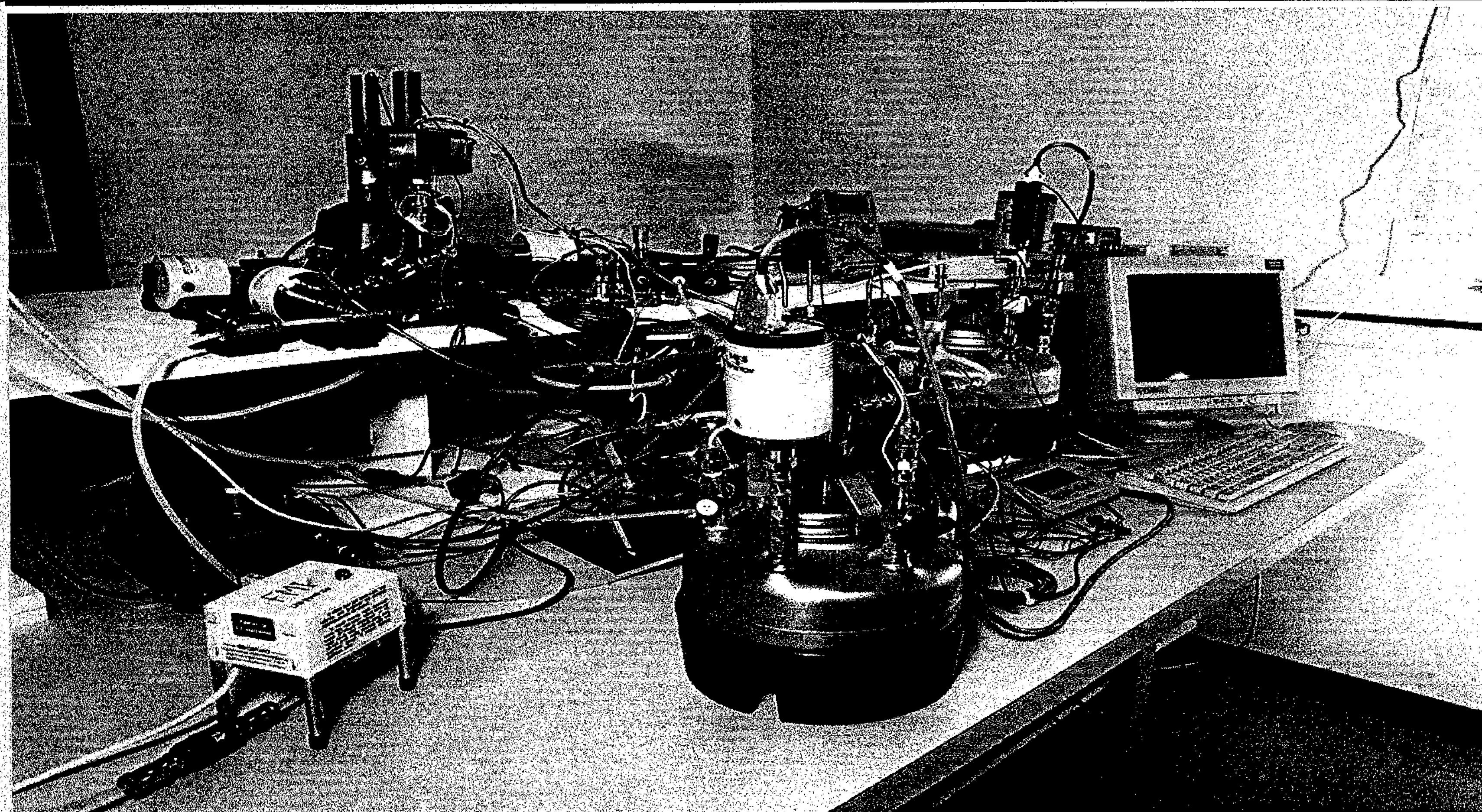
MICROTECHNOLOGY-BASED HP BENCHTOP TEST LOOP



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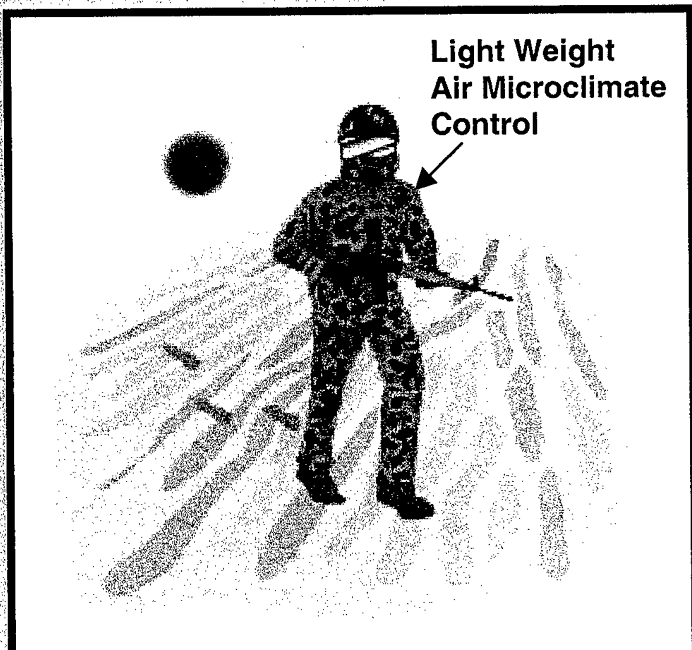
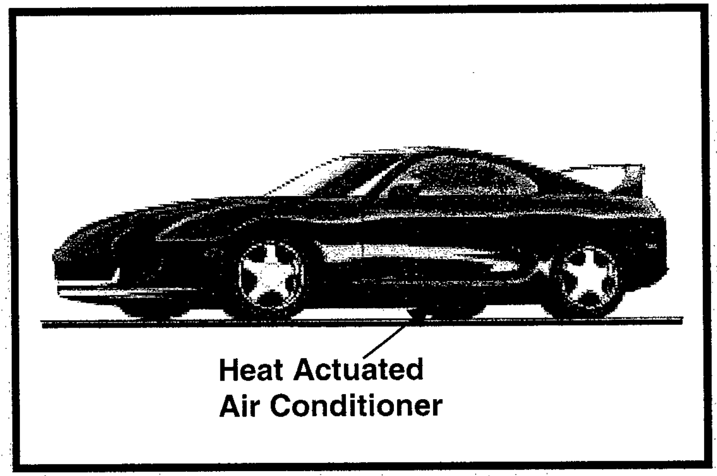
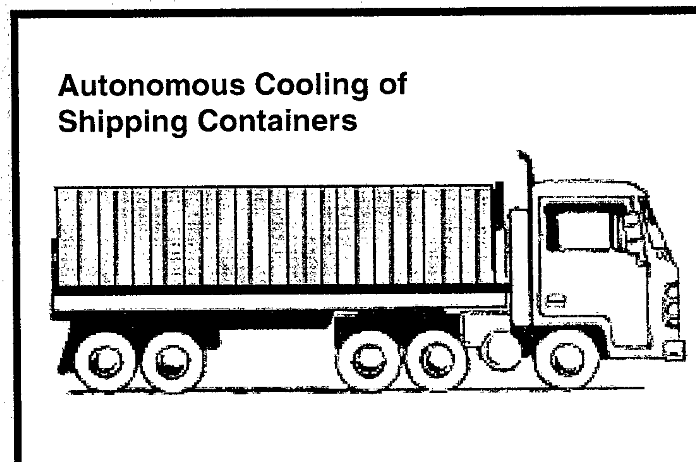
MICROTECHNOLOGY-BASED HEAT PUMP - APPLICATIONS







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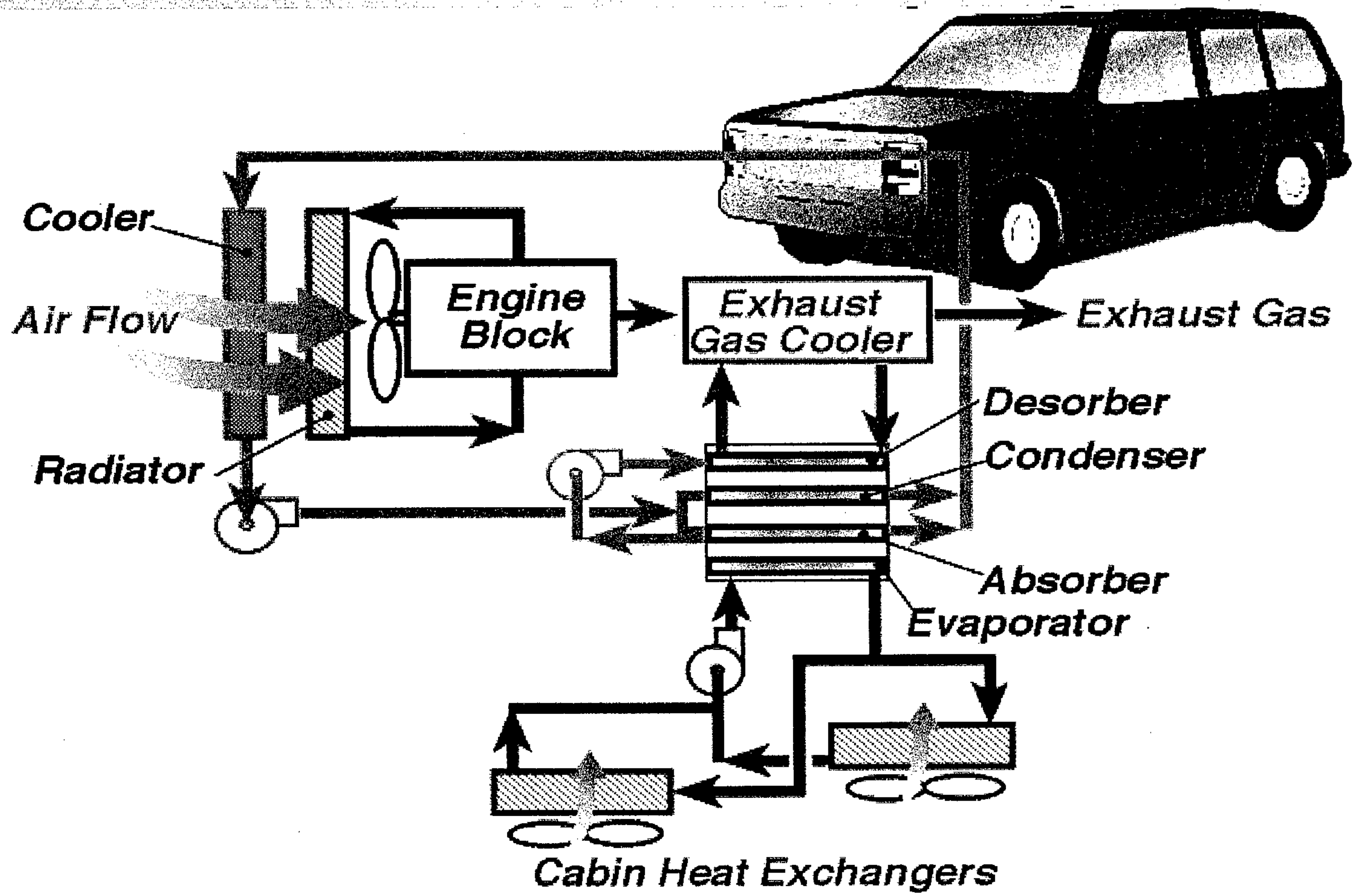
MICROTECHNOLOGY-BASED HEAT PUMP : AUTOMOBILES



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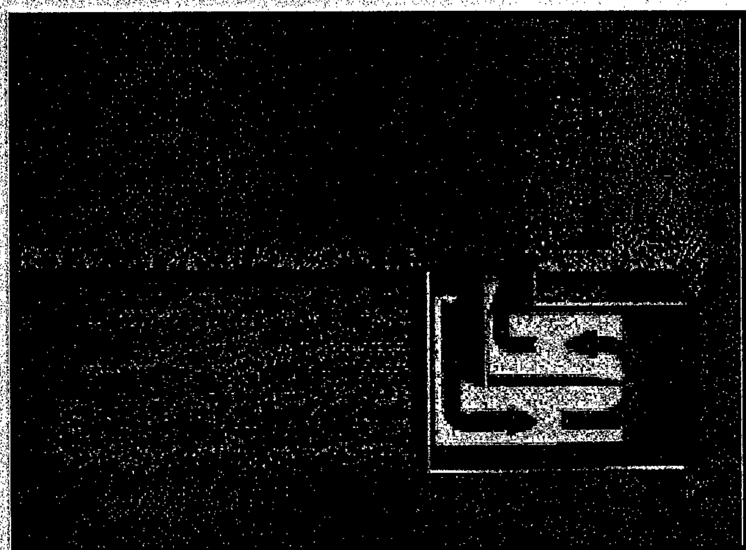
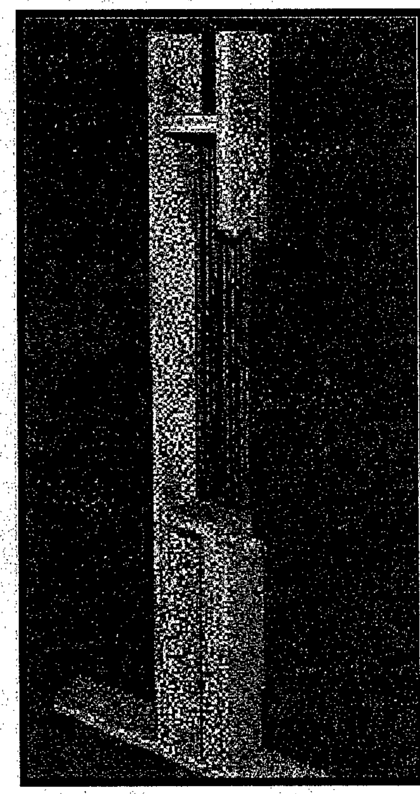
MICROTECHNOLOGY-BASED HEAT PUMP : BUILDINGS



In-Joists



In-Wall

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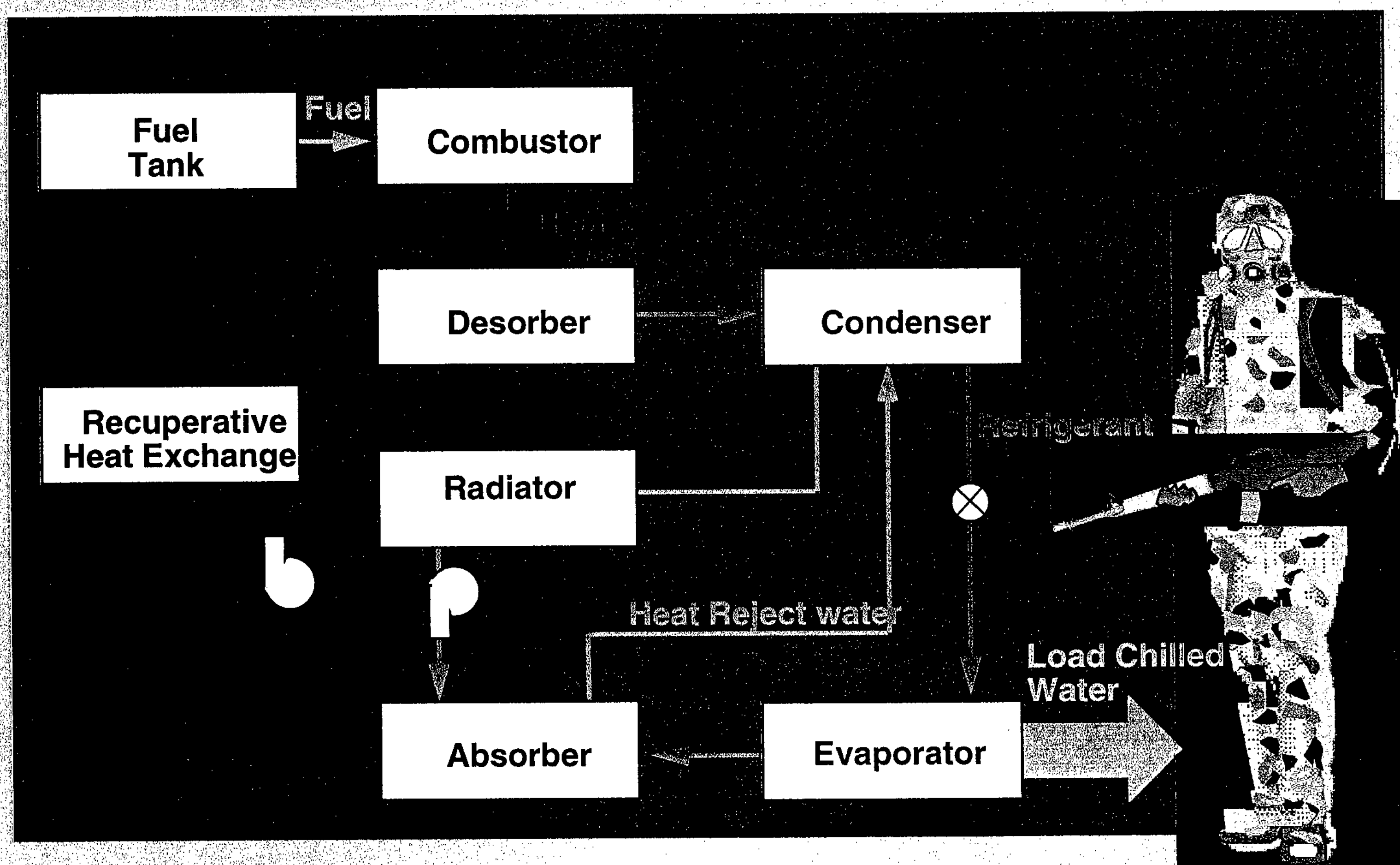
DARPA PROGRAM
MANPORTABLE ABSORPTION CHILLER



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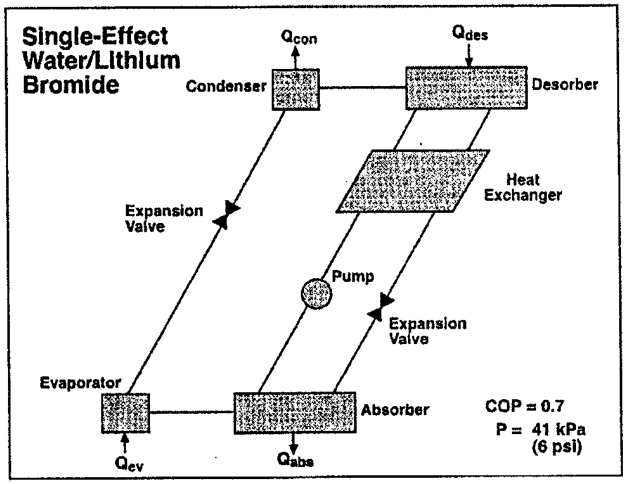
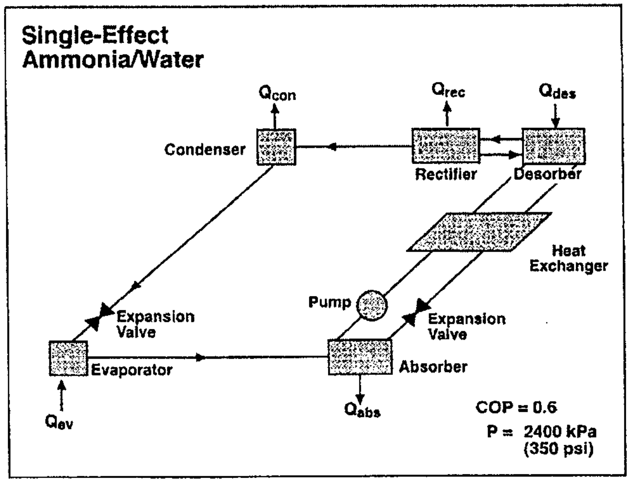
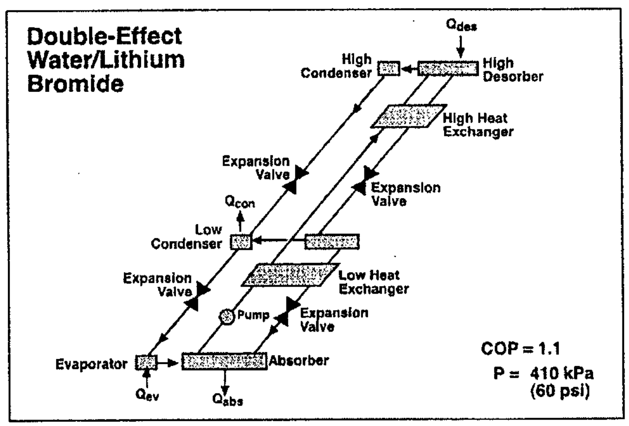
KEY DESIGN DECISION - WHAT ABSORPTION CYCLE?







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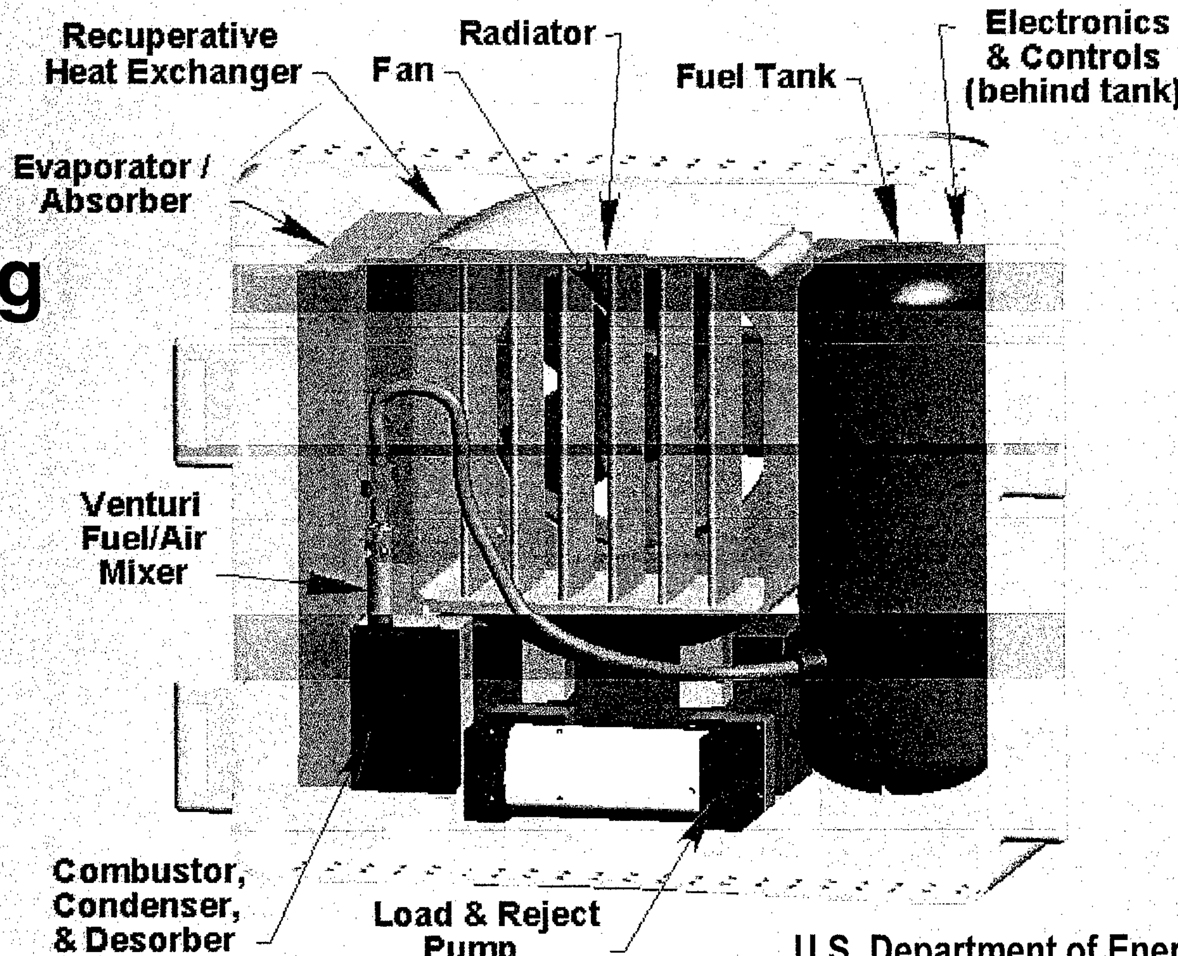
DARPA MANPORTABLE COOLER

5.1 kg

350 W cooling for 8 hours



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CONCLUSIONS

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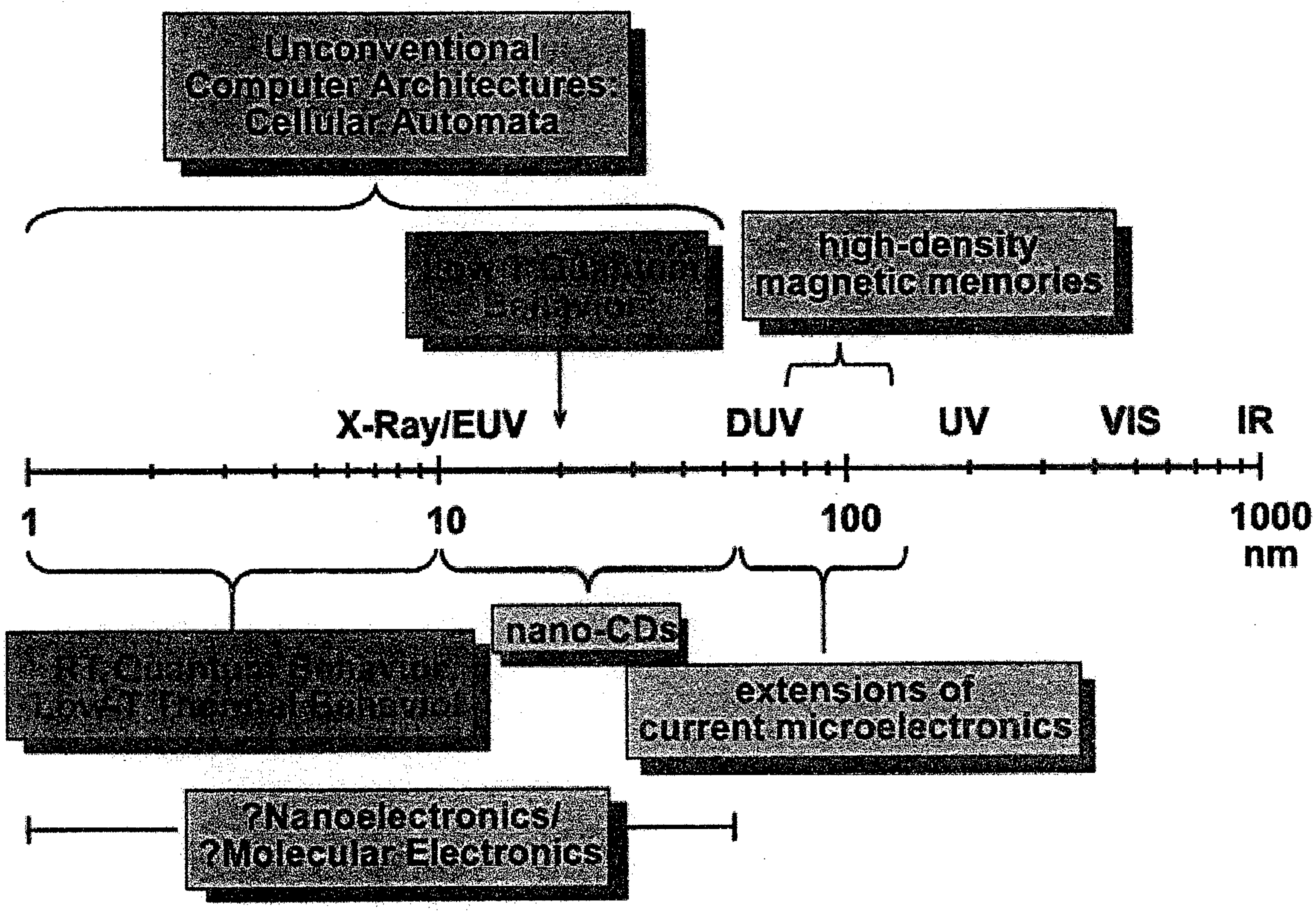
The Scale of the Problem

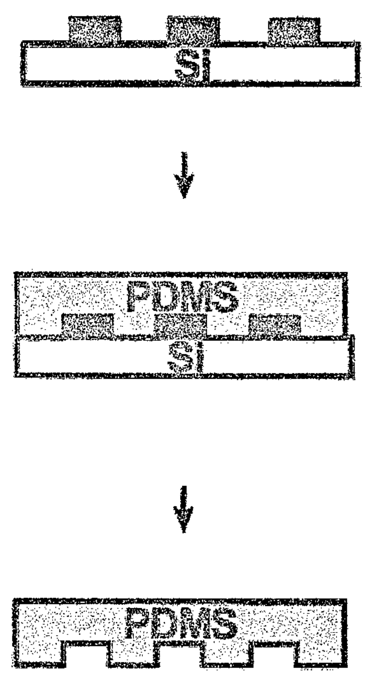


Soft Lithography

- Nanoreplication
- Single layer, <1 μm fab
- Large area printing at μm scale
- Curved surfaces
- Organic functional group control

- MEMS
- Sensors
- Optics
- Microfluidics
- Biochemistry / cell biology

Preparation of the Stamp/Mold/Optical Element

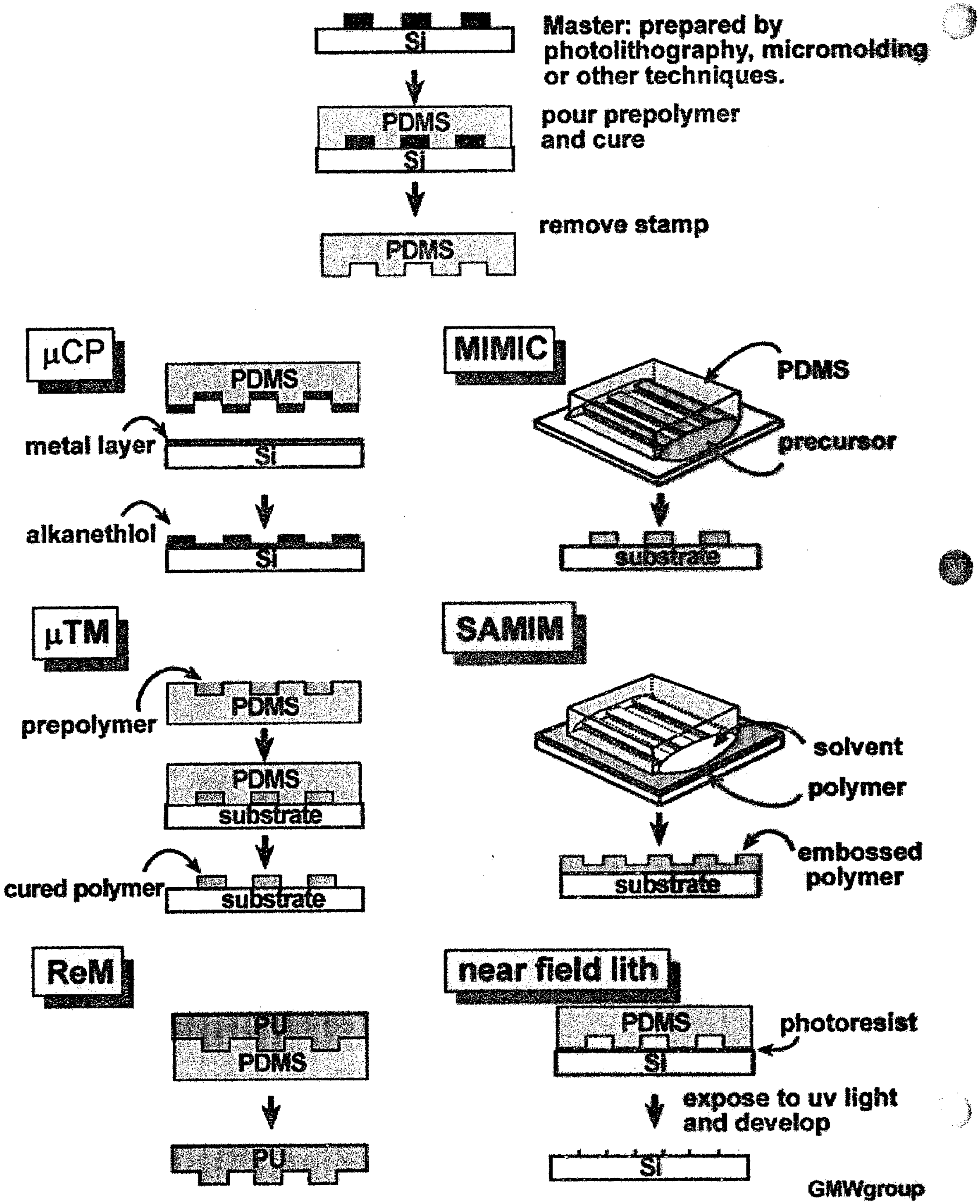


Master: prepared by photolithography, micromolding, e-beam writing, or other techniques

pour prepolymer and cure

remove stamp

Techniques of Soft Lithography



Soft Lithography

Strengths

- 3D, curved surfaces, inside surfaces
- Non-photolithographic
- Rapid Prototyping (>50 µm → 10 µm?)
- New materials (polymers, metals, ceramics)
- Low capital/operating cost
- <100 nm features
- Large-area
- (Electrochemistry)

Weaknesses

- Defect levels
- Distortion/Runout
- Alignment in multilevel fabrication

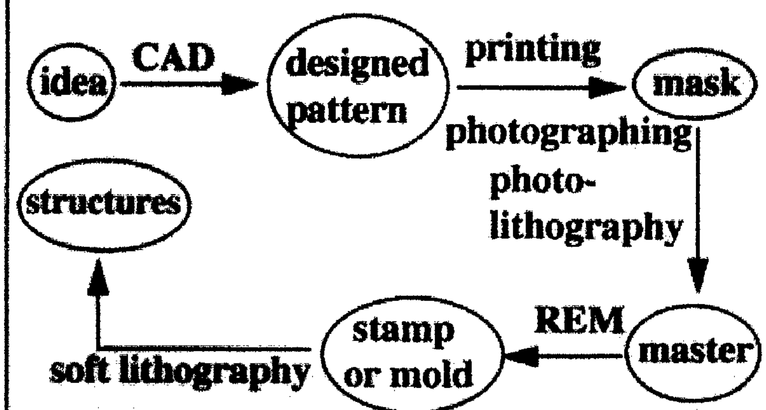
Rapid Prototyping Using Soft Lithography

Tao Deng, Dong Qin, and George M. Whitesides
Department of Chemistry, Harvard University

Objective

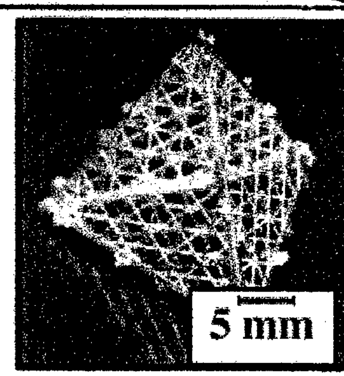
- **Development of new methods and materials for rapid prototyping microstructures for chemistry, biology and materials laboratories**

Technical Approaches

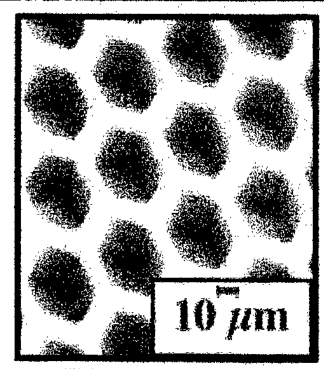


Accomplishments

- **Rapid prototyping complex microstructures (>20 μm) using printed film**
- **Rapid prototyping complex microstructures (>10 μm) using microfiche**



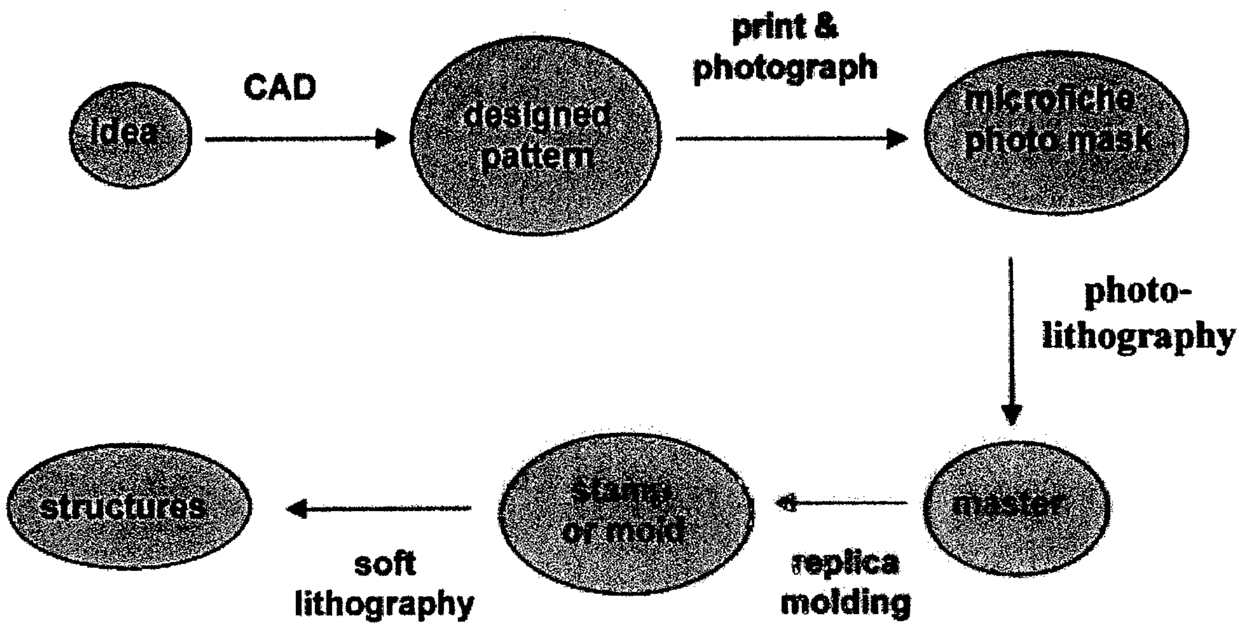
Tetrahedral Cage

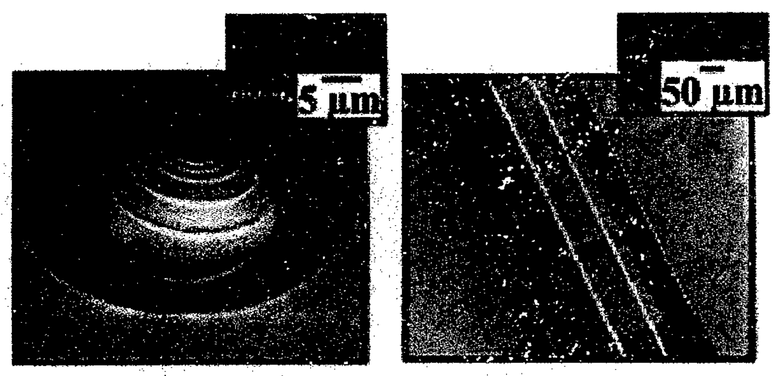


Honeycomb

Rapid Prototyping Using Microfiche as Photomask

GMWgroup

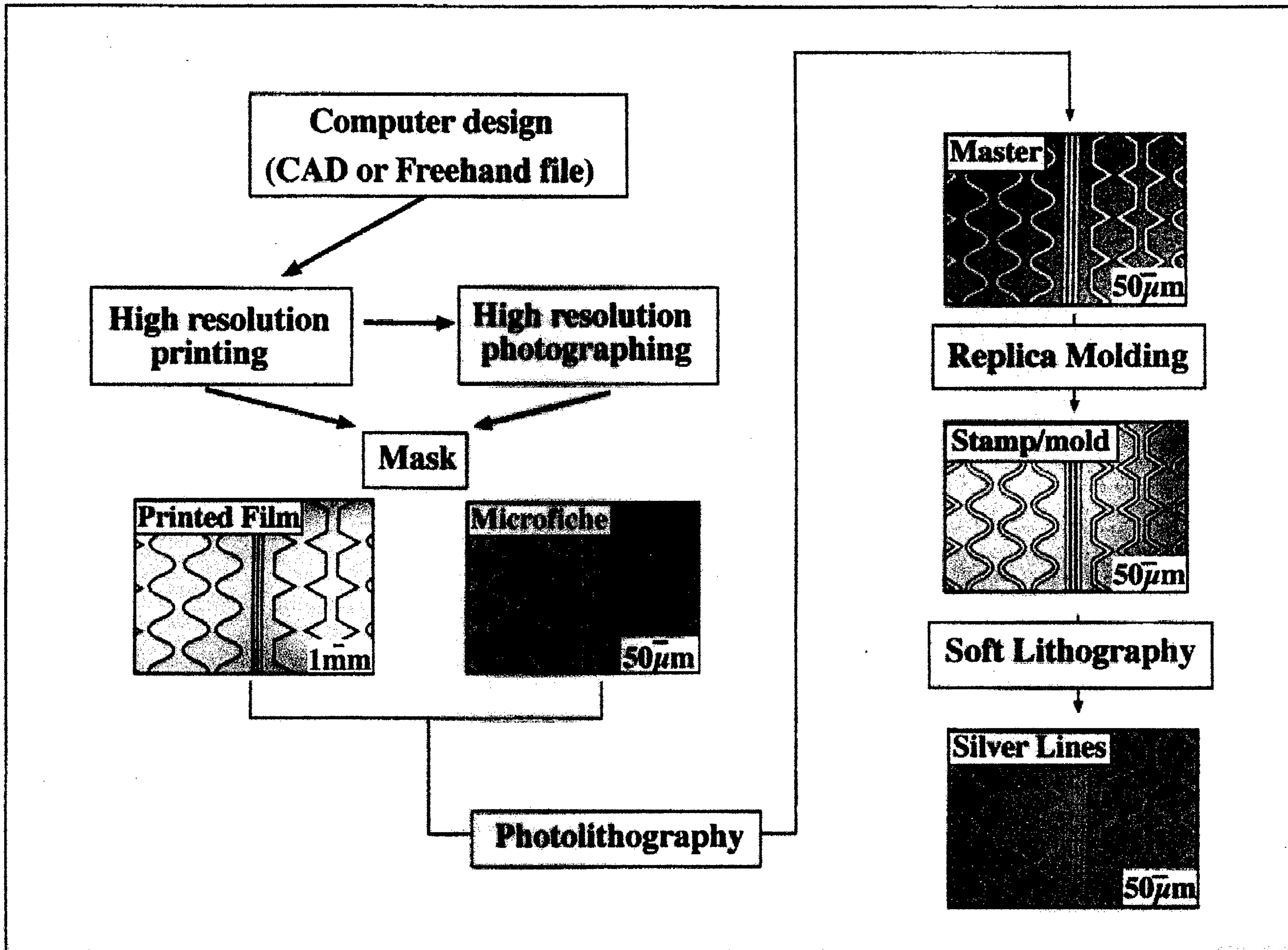




Microspring

Honeycomb

Process for Rapid Prototyping Using Soft Lithography



Microfluidic Devices in Organic Polymers

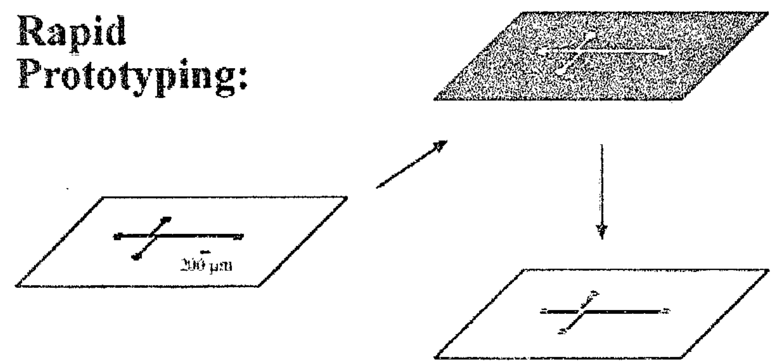
Cooper McDonald, Janelle Anderson, Olivier Schueller, and George M. Whitesides, Harvard University

Objectives

- Develop methods for the rapid prototyping of complex devices
- Design, fabricate, and test new components

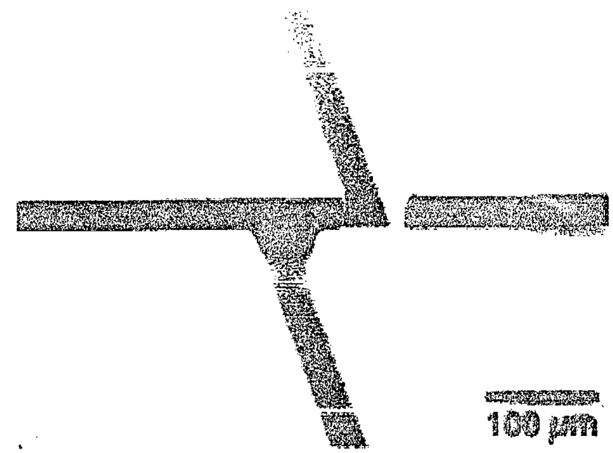
Technical Approach

Rapid Prototyping:



Accomplishments

- capillary electrophoresis in PDMS chip
- 3D systems of channels
- pumps, valves



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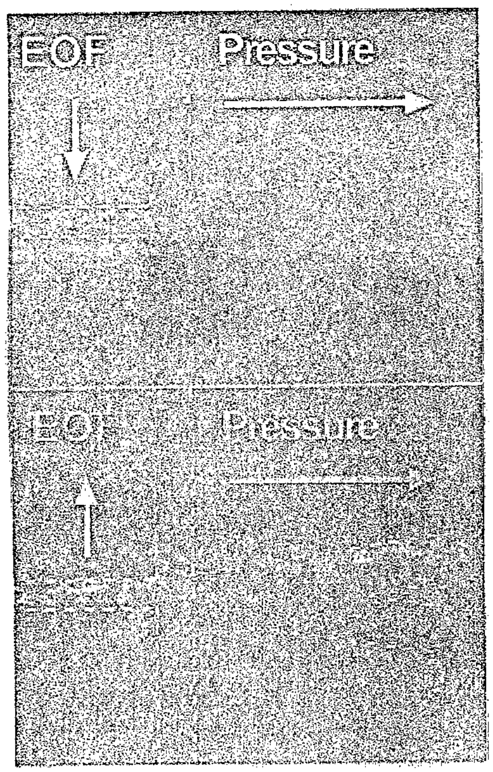
A



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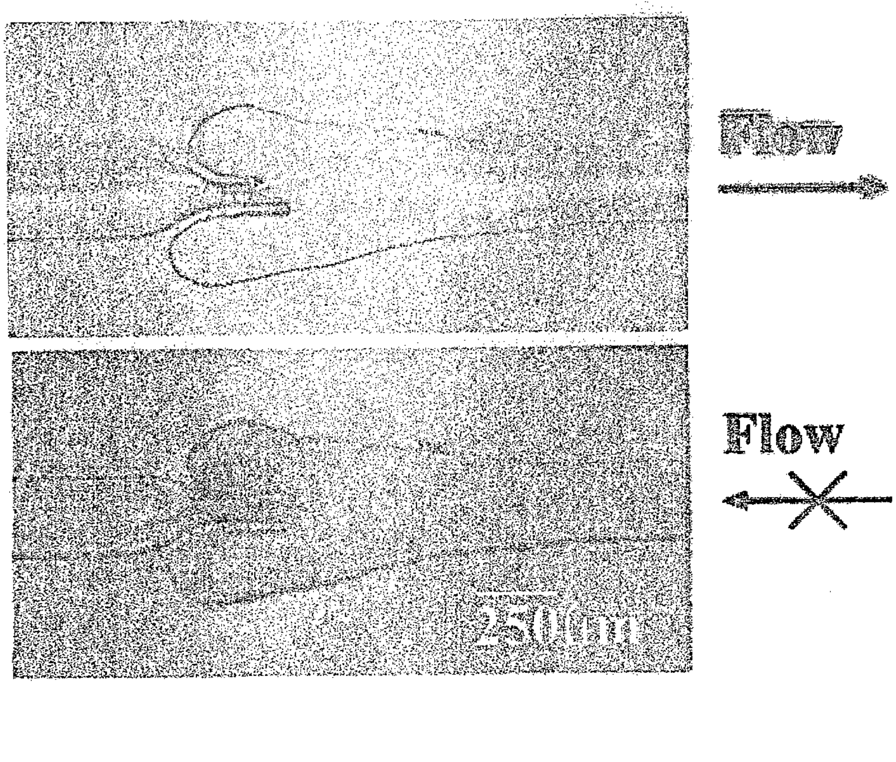


Fabrication of Optical Components based on Microfluidic Devices

Olivier Schueller, David Duffy, John Rogers, Scott Brittain, Stephen Smith, Mara Prentiss, George M. Whitesides, Harvard University

Objective

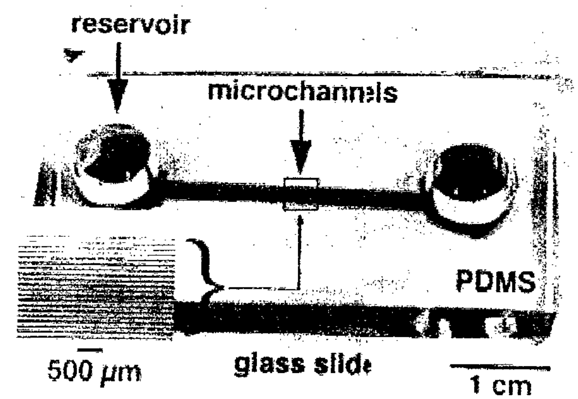
- to demonstrate the fabrication of optical devices and microfluidic devices by soft lithography
- to integrate optics and microfluidics (sensing and actuating)

Technical Approach

- replica molding of PDMS
- sealing by plasma oxidation
- liquids with specific optical properties (index of refraction and absorption)

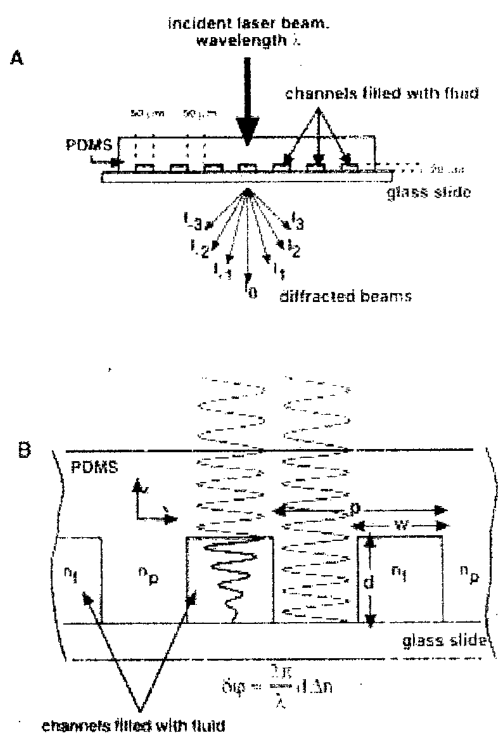
Accomplishments

- elastomeric light valves
- liquid-core waveguides
- reconfigurable diffraction gratings

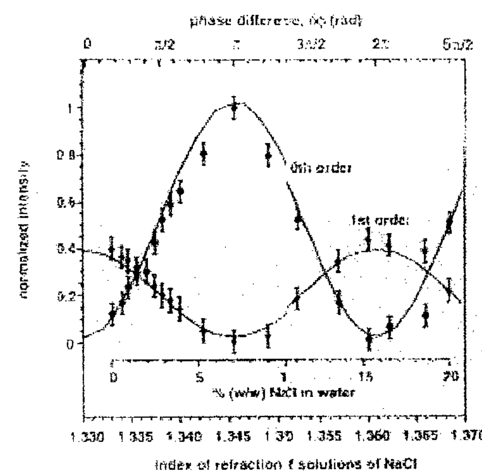


Microfluidic Diffraction Gratings

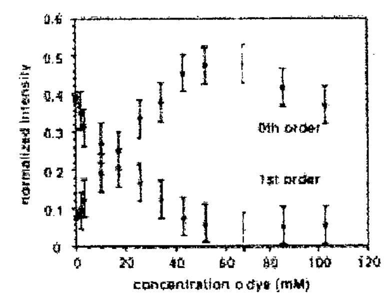
Olivier Schueller, David Duffy, John Rogers, Scott Brittain, George M. Whitesides, Harvard University



index of refraction

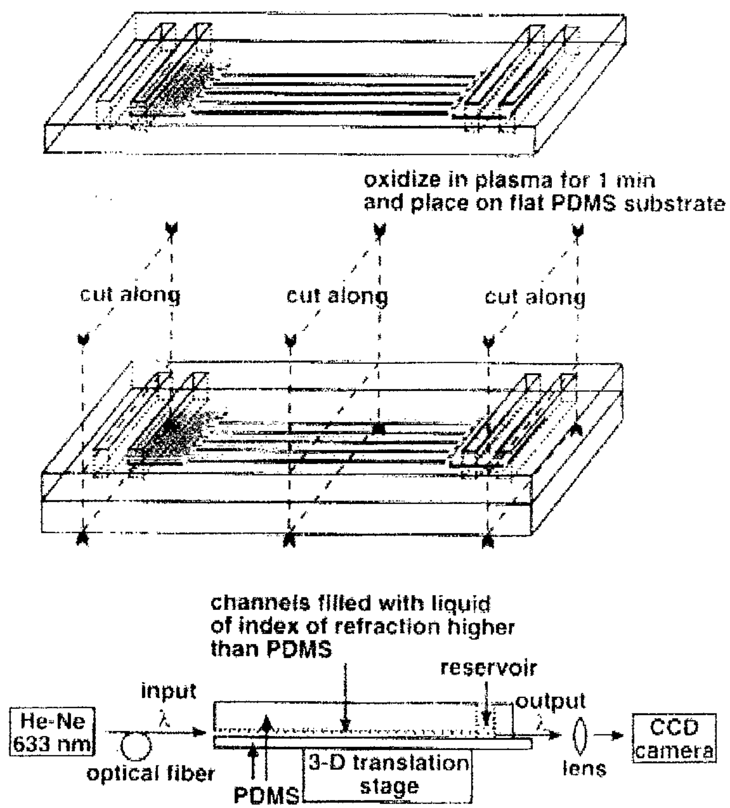


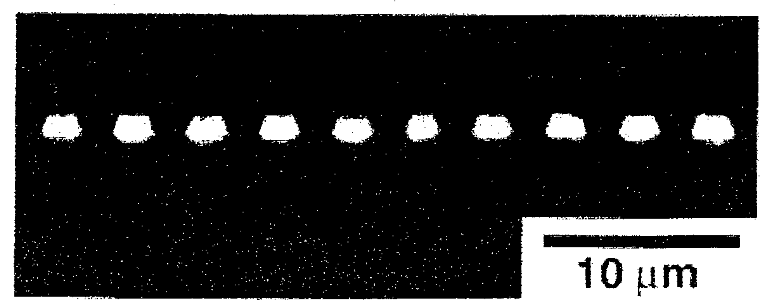
absorption

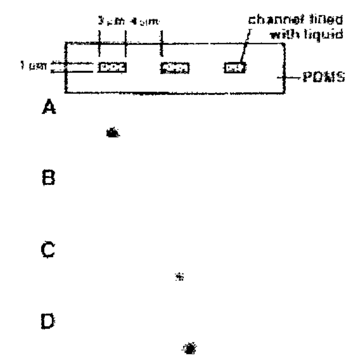


Liquid-Core Waveguides

Olivier Schueller, Xiao-Mei Zhao, Stephen Smith
Mara Prentiss, George M. Whitesides, Harvard University







Laminar Flow Patterning: Fabrication of Structures Inside Microfluidic Channels

GMW group

Reynolds number (*Re*) < 1000

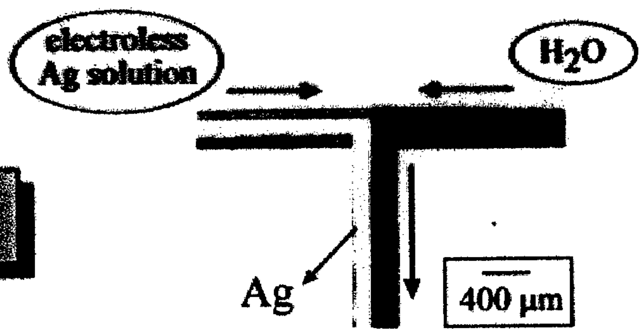
$$\boxed{Re = \frac{l.v.\rho}{\eta}}$$

l = diameter
v = flow velocity
ρ = density
η = viscosity

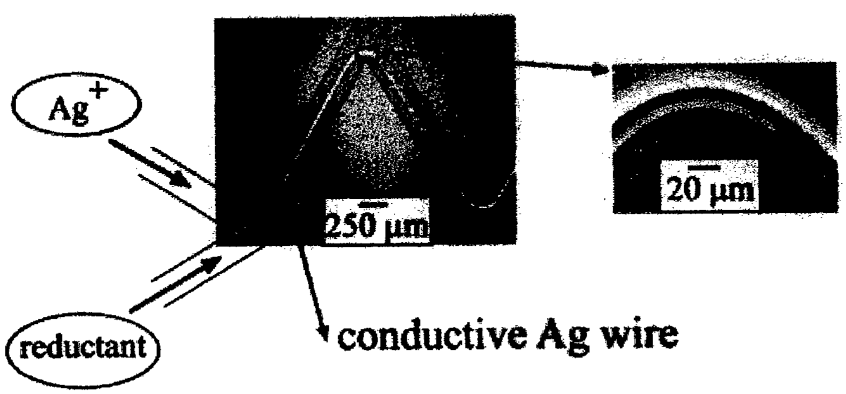
Etching - SiO_2
- metals (Au, Ag, Cr, ...)

Deposition - metals (electroless Ag, Cu, ...)
- thiols that form SAMs
- polymers
- biomaterial (proteins, cells)

From Separate Phases
channel in PDMS



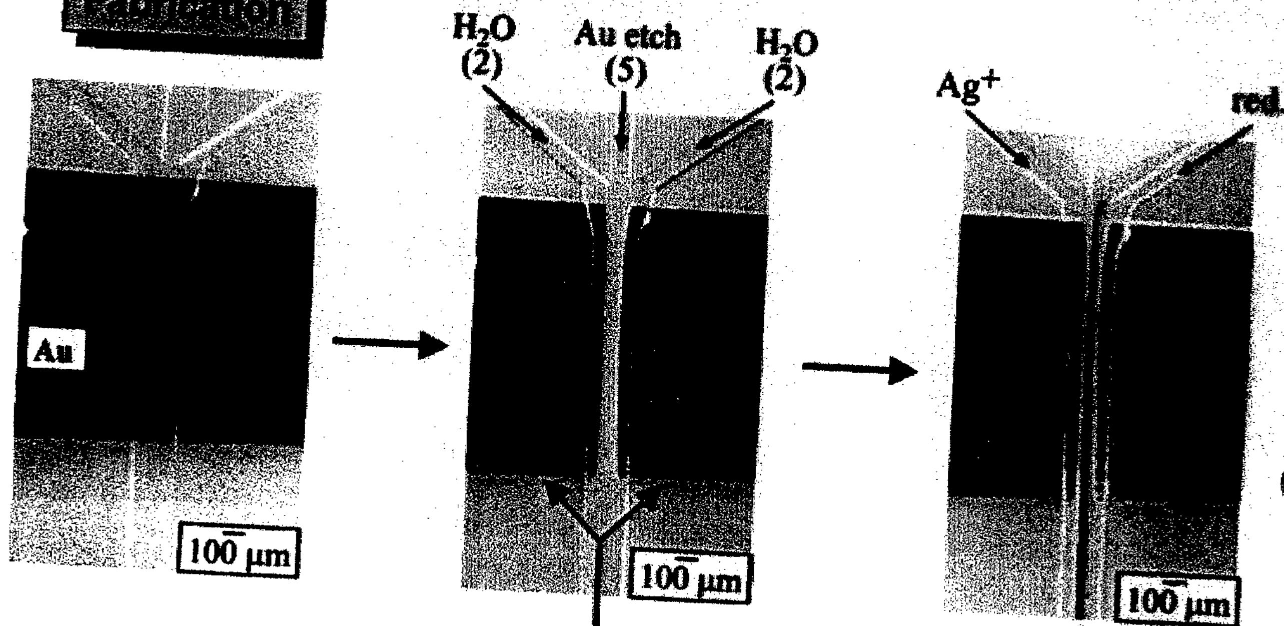
At the interface of Phases
channel in PDMS on glass



A Three-electrode System Made by Laminar Flow Patterning

GMW group

Fabrication

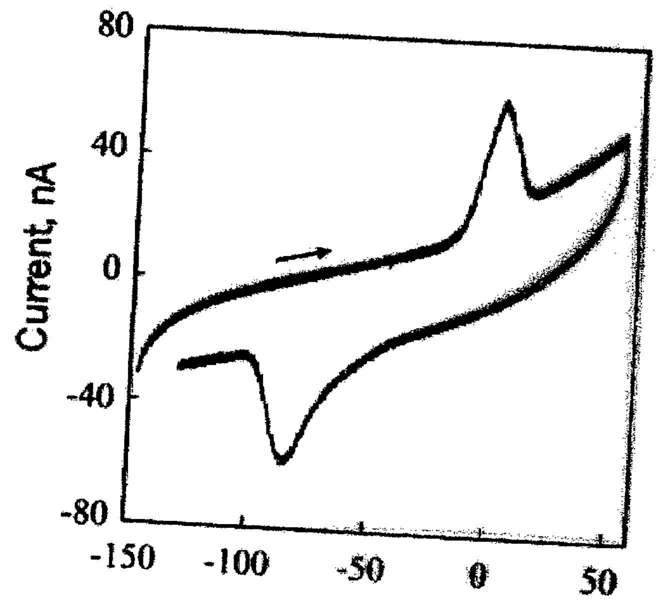


PDMS channel on a glass substrate

counter and *working* electrodes

Ag wire *reference* electrode

Cyclic Voltammogram of $Ru(NH_3)_6Cl_3$ Drop of 25 nL, 1 mM in H_2O



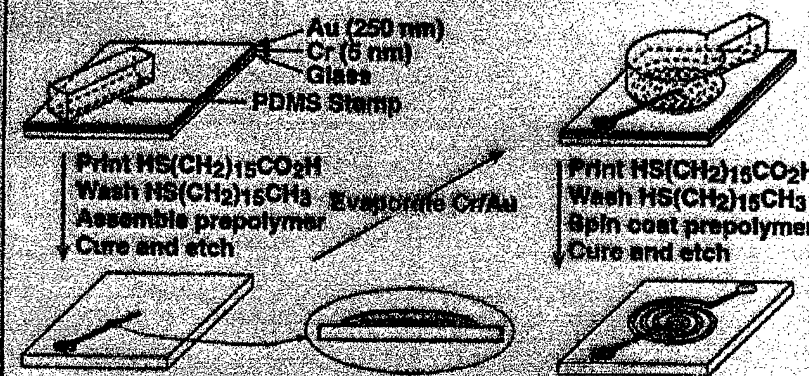
Fabrication of Surface Coil Inductors by Self-Assembly

Andrew J. Black, Joseph H. Thywissen,
Mara Prentiss and George M. Whitesides, Harvard University

Objectives

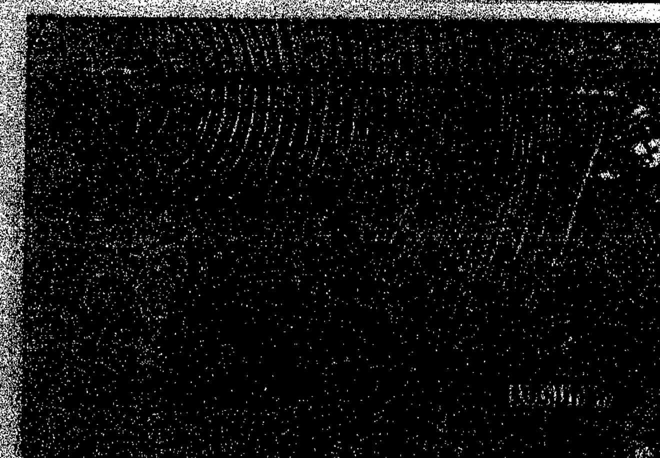
- Use self-assembly to fabricate two level structures with crossed wires
- Demonstrate that the wires are electrically isolated
- Show these structures can be used as electrically functional components

Technical Approach



Accomplishments

- Fabrication of a surface coil inductor using **self-assembly**
- Wires in two layers are **electrically isolated**
- Measured an inductance of 2.8 +/- 0.2 μH (predicted value is 2.4 μH). Magnetic field is 40 Gauss/Amp.



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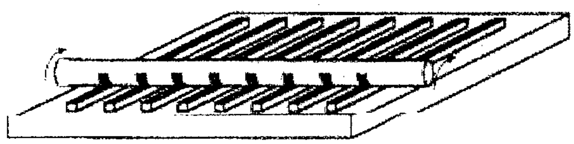
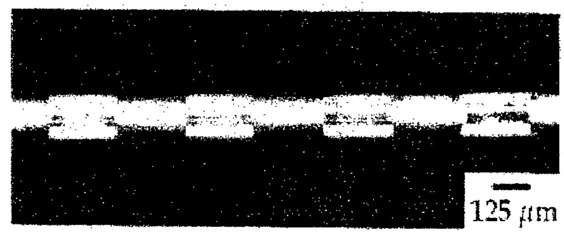
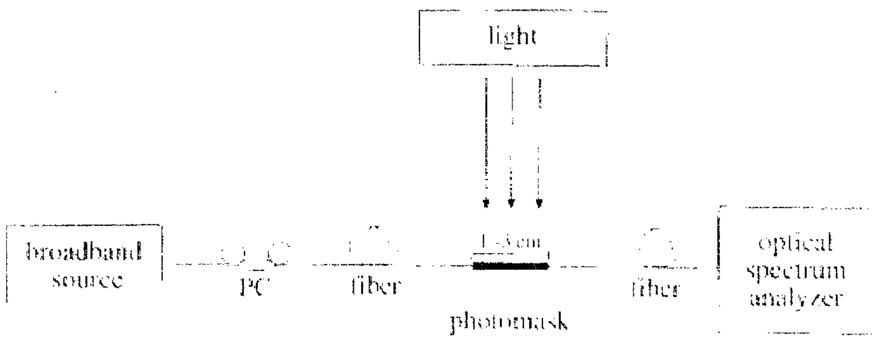
Fabrication and Characterization of In-Fiber Grating Attenuators formed using Amplitude Photomasks formed by μCP

use μCP to form opaque lines on exterior of fiber

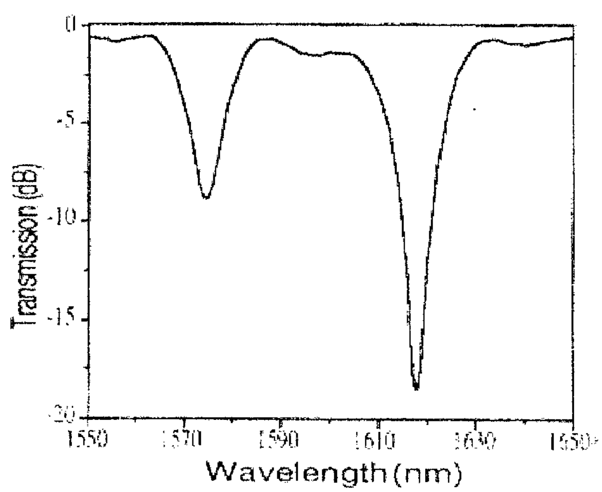




expose resulting structure to uv light



measure performance of attenuator formed by exposure of an unloaded, printed fiber to uv light for 24 hours

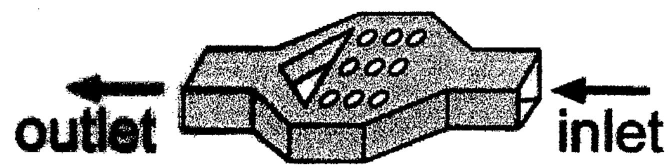


Metallic Heat Exchangers

Francisco Arias, Bing Xu, and George M. Whitesides
Department of Chemistry, Harvard University

- *Objectives:* new processes, use sacrificial polymer frameworks to construct three-dimensional metallic structures.
- *Applications:* cooling systems for electronic components.

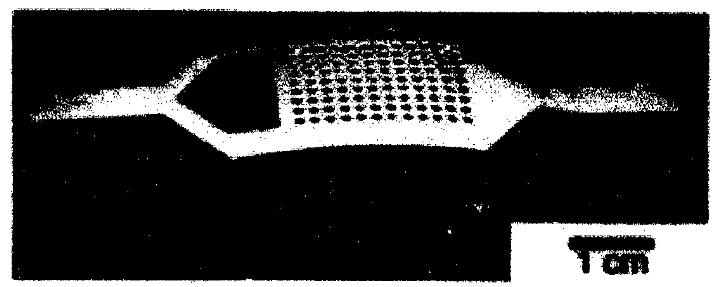
Design



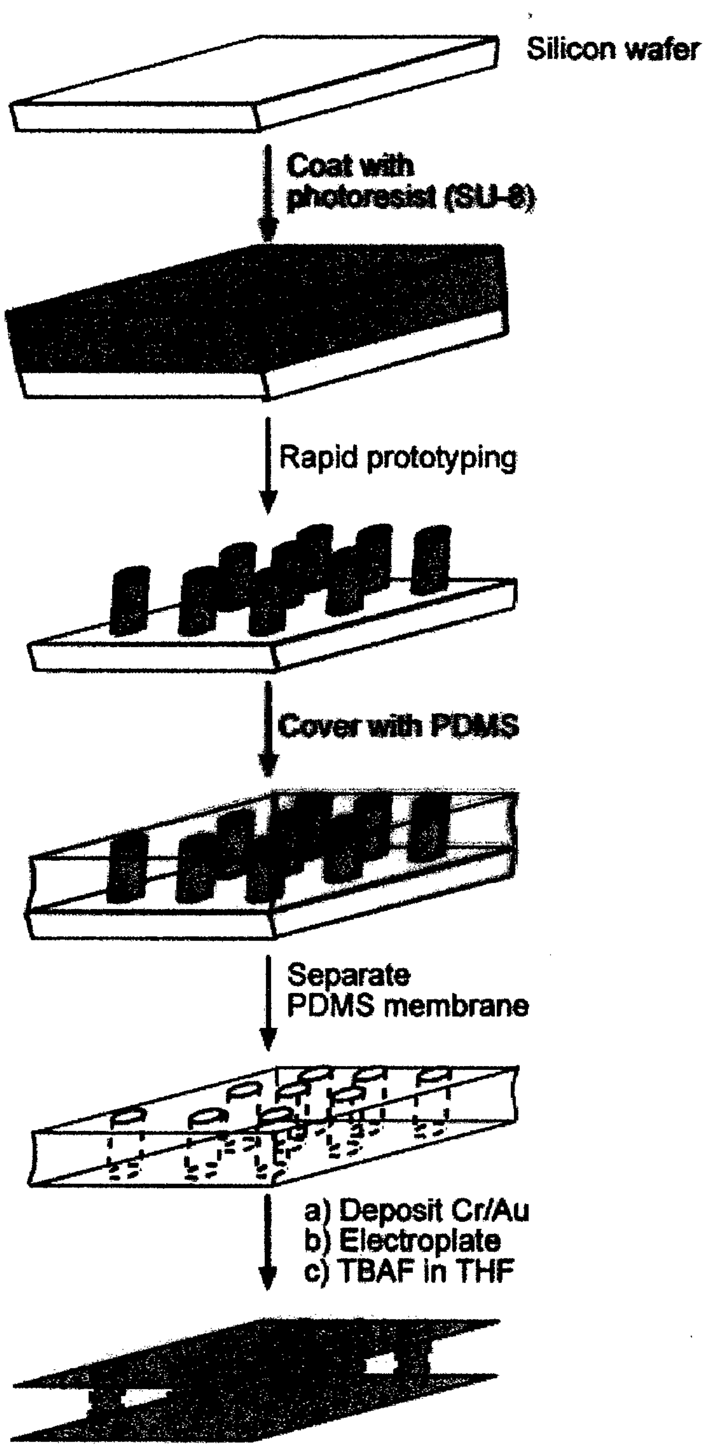
- *Technical Approach:*
  Polymers
  Photolithography
  Vapor deposition
  Electroplating

- *New Achievements:* fabricated nickel and copper thermal modules with 200-500 μm wide channels.

Nickel Heat Exchanger



HOLLOW METALLIC STRUCTURES



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Honeycomb Microcomposites

Bing Xu, Francisco Arias, George M. Whitesides, Harvard University*

Objectives:

Fabrication of high strength-to-weight ratio materials

Applications:

UAV, hard disk drive arms, and other MEMS devices

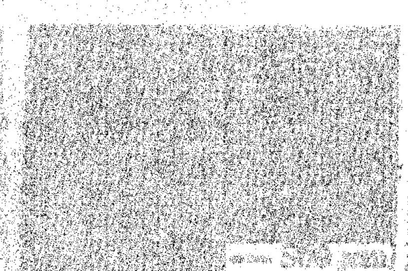
Technical Approach:

- soft lithographies:
  - rapid prototyping
  - μTM
  - μEmbossing
  - electroplating
- polymers, metals, ceramics

Past Accomplishments:

Developed methods for fabricating high aspect ratio honeycomb structures and fabricated honeycomb microcomposites

polymer



metal

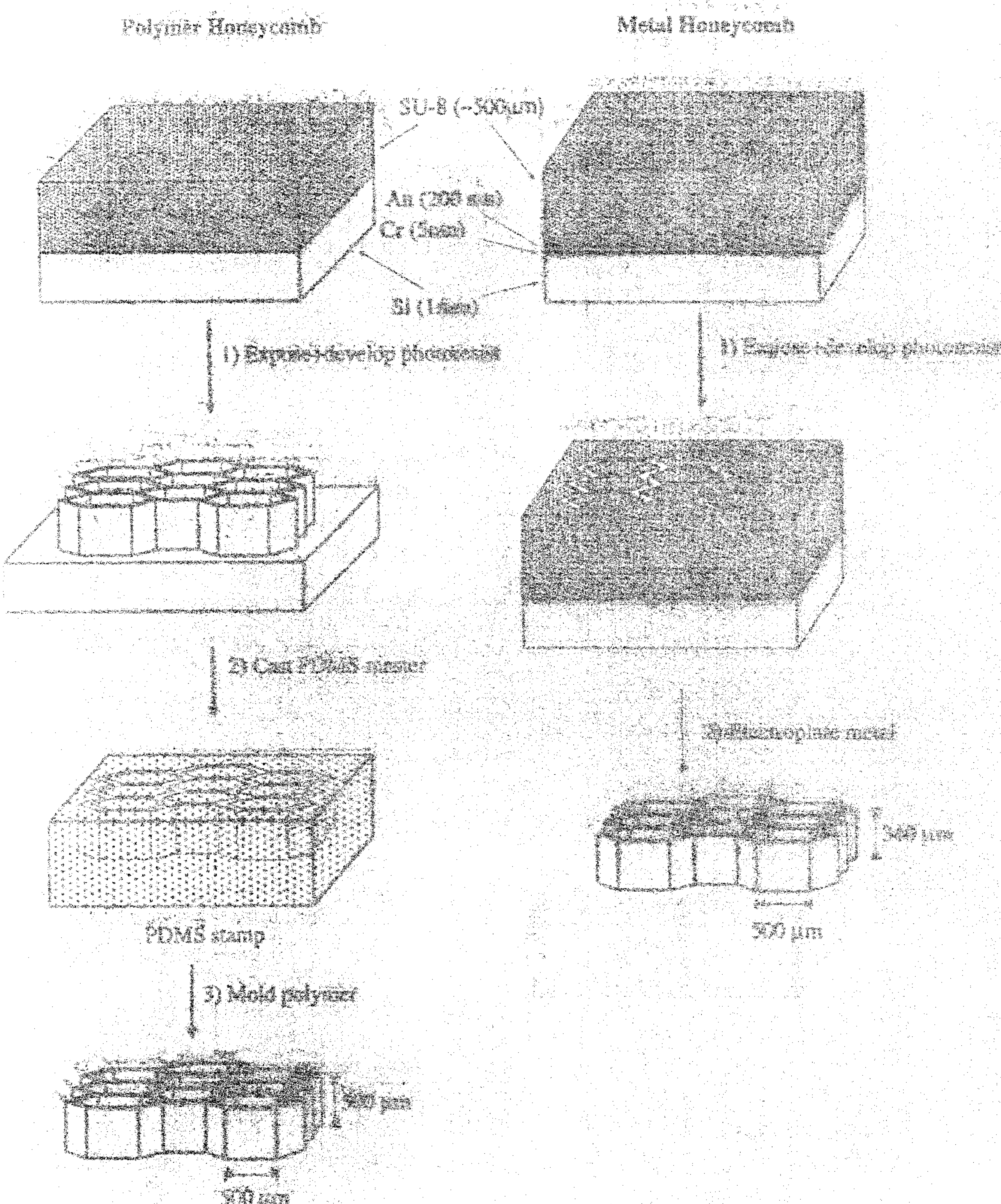

Polymer Honeycomb
Metal Honeycomb
SU-8 (~500μm)
Cr (5nm)
PDMS stamp
3) Mold polymer
500 μm
500 μm

Figure 1

THE USE OF SOFT LITHOGRAPHY TO FABRICATE MICROELECTRONIC DEVICES AND CIRCUITS

Tao Deng, Junmin Hu, Noo Li Jeon, and George M. Whitesides
Department of Chemistry, Harvard University

Objective

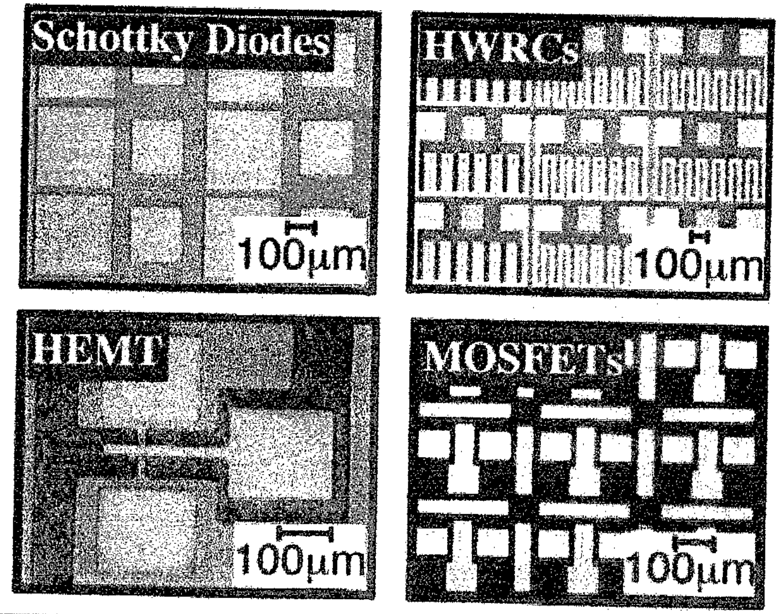
- **To fabricate functional microelectronic devices and circuits using soft lithography**

Accomplishments

- **Fabrication of Si Schottky diodes and half-wave rectifier circuits**
- **Fabrication of functional GaAs/AlGaAs HEMTs and Si MOSFETs**
- **Demonstration of compatibility of soft lithography with standard semiconductor processing**

Technical Approach

- **Soft Lithography**



Large-Area MIMIC

Noo Li Jeon, Insung Choi, Bing Xu, and George Whitesides, Harvard University

Objectives

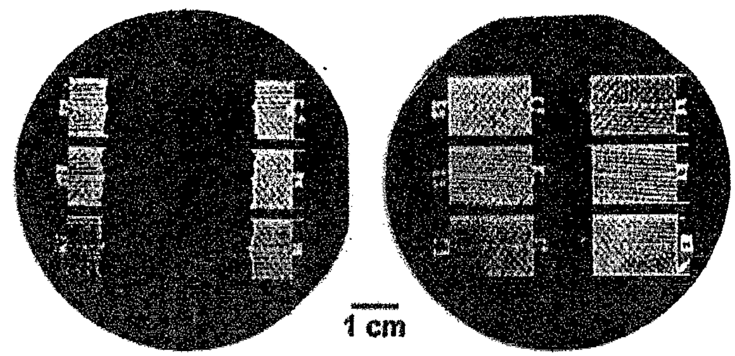
- Rapid patterning of large areas.
- Patterning functional polymers.
- Patterning on flexible substrates.
- Patterning on curved substrates.

Accomplishments

- Patterned a 3-inch wafer in 15 seconds with 25 µm wide lines.
- Patterned conducting polymers on 3-inch wafers.
- Patterned 25 µm wide lines on thin flexible polyimide sheets.
- Patterned 25 µm wide lines on

Technical Approach

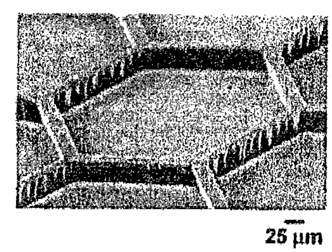
- Vacuum-Assisted MIMIC.
- Multi-point inlet design.



w/o Vacuum
After 15 min.

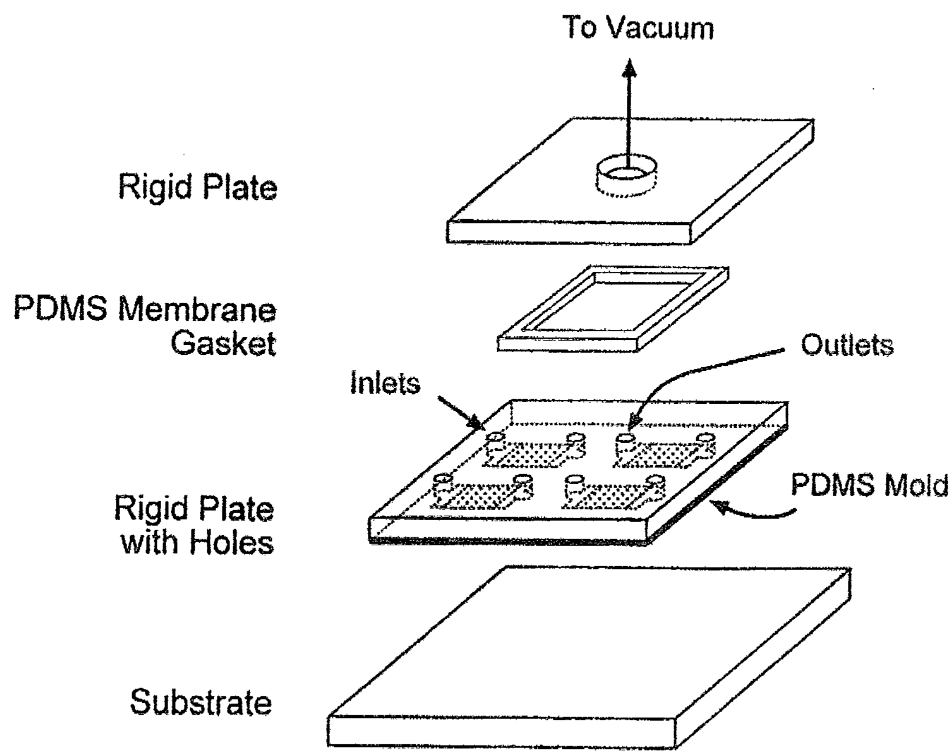
with Vacuum
After 15 sec.

Height: 50 µm
Width: 25 µm

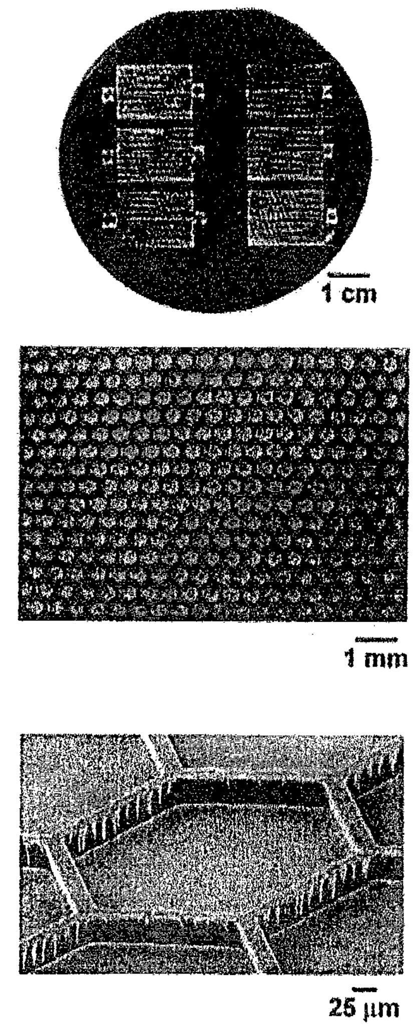


Large-Area MIMIC

Noo Li Jeon, Insung Choi, Bing Xu, and George Whitesides, Harvard University



Schematic of the Setup used in Vacuum-Assisted MIMIC



A 3-inch Si Wafer Pattered by

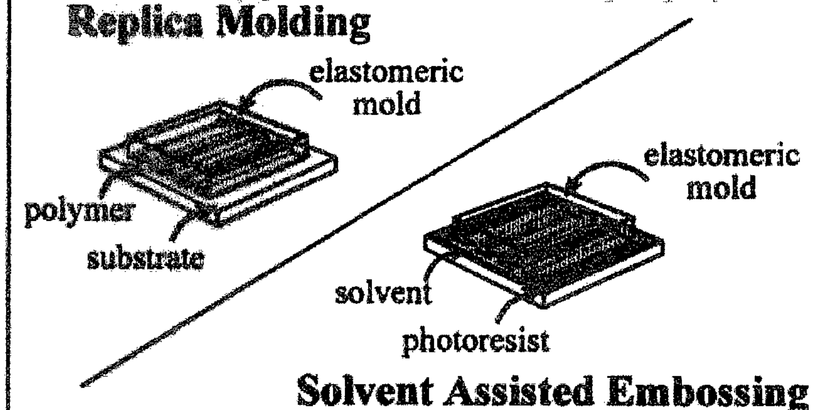
Soft Lithography: Nanomolding

Y. Xia, E. Kim, X.-M. Zhao, K. E. Paul and G. M. Whitesides
Department of Chemistry, Harvard University

Objective:

To provide simple and economical method for patterning < 100-nm features, especially from a serial process, high cost master.

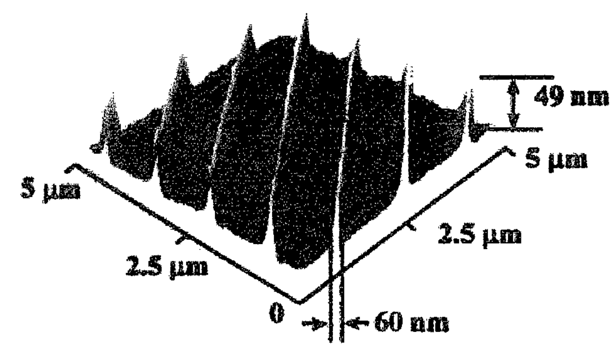
Technical Approach: Soft Lithography



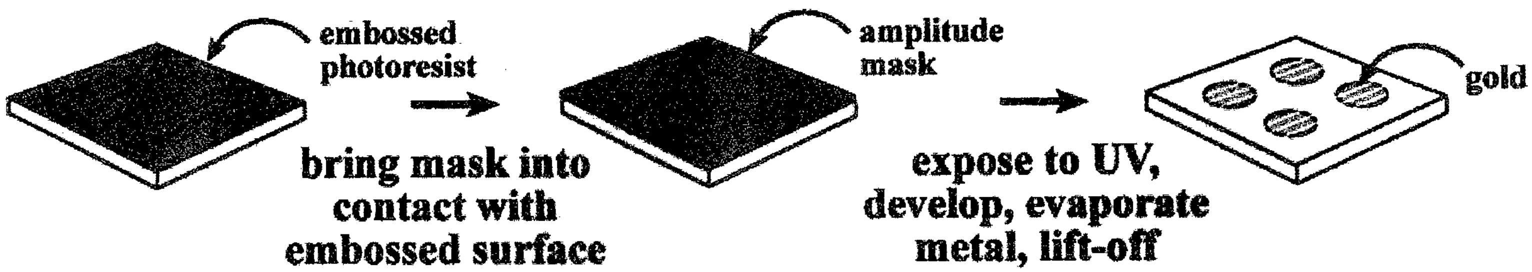
Accomplishments:

- Production of multiple copies from a single master
- Use of elastomer preserves fragile features
- Areas as large as 6 cm^2 have been patterned
- Features as small as 30 nm molded

Features Produced by Replica Molding

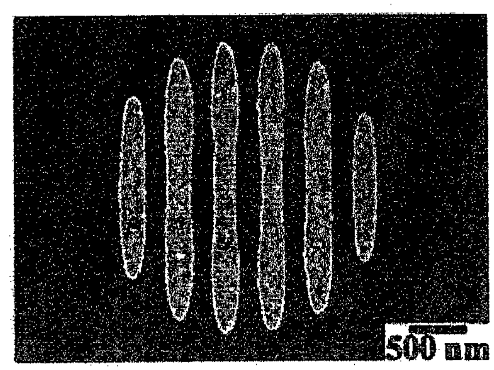


Embossed Resist Combined with an Amplitude Mask



Photoresist on Si after exposure and development

Au on Si after lift-off



GMW 11/98

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Fabrication of Glass Microstructures by Sol-Gel Chemistry

Olivier Schueller, Christian Marzolin, Stephen Smith, Mara Prentiss,
George M. Whitesides, Harvard University

Objective

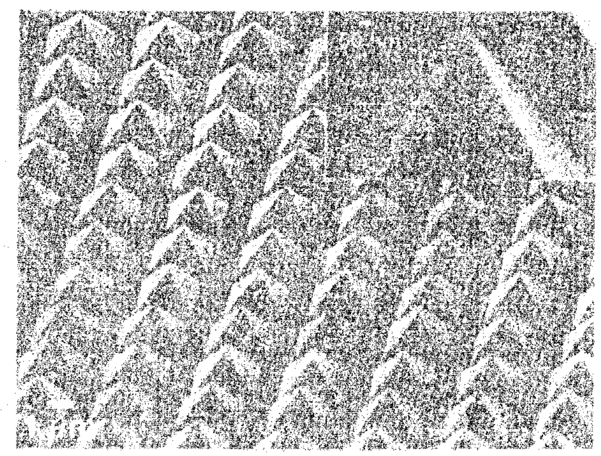
- to demonstrate the fabrication of glass microstructures by soft lithography
- to control the physical properties of these microstructures

Technical Approach

- replica molding using PDMS
- sol-gel chemistry
- hybrid materials

Accomplishments

- large area structures
- submicron features
- single-mode waveguides
- diffractive optical elements



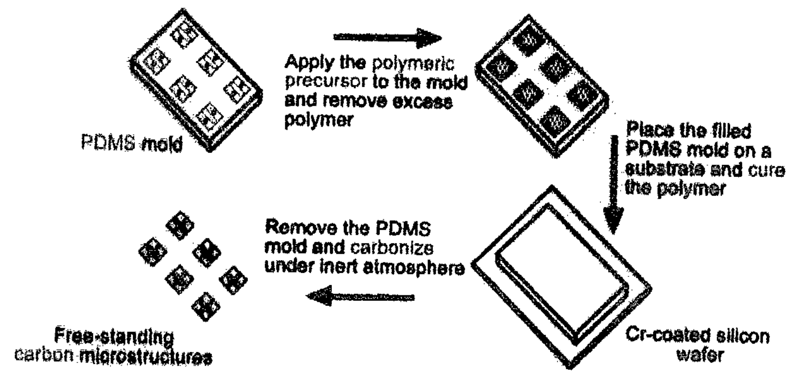
Carbon MEMS

Scott Brittain, Olivier Schueller, Paul Kenis, Bartosz Grzybowski, George M. Whitesides,
Harvard University

Objectives

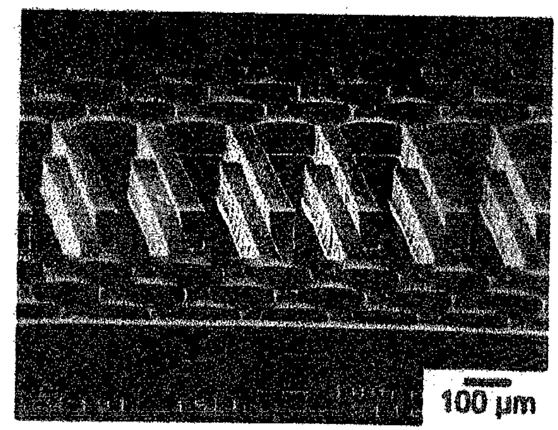
- To fabricate MEMS at lower cost than silicon micromachining
- carbon
  - chemically inert
  - thermally stable

Technical Approach: µTM



Accomplishments

- Fabricated high aspect-ratio (~7:1) features in glassy carbon
- Fabricated 2-level carbon microstructures
- Demonstrated electrostatic actuation in carbon microstructures



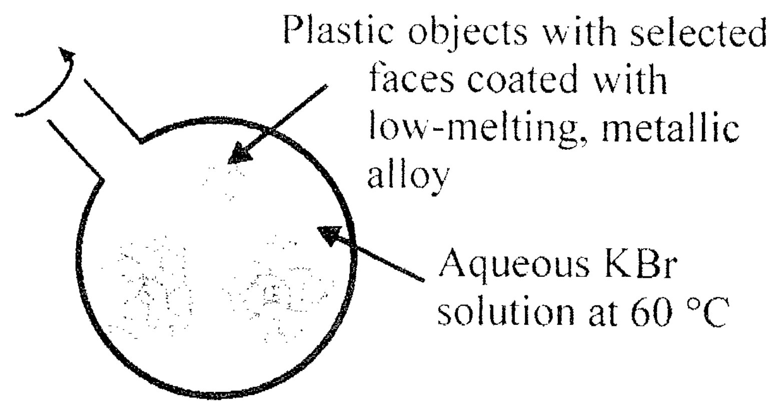
Self-Assembly of Open, 3D, Lattice Mesostructures

Tricia L. Breen, Joe Tien, Scott Oliver and George M. Whitesides
Department of Chemistry, Harvard University

Objective:

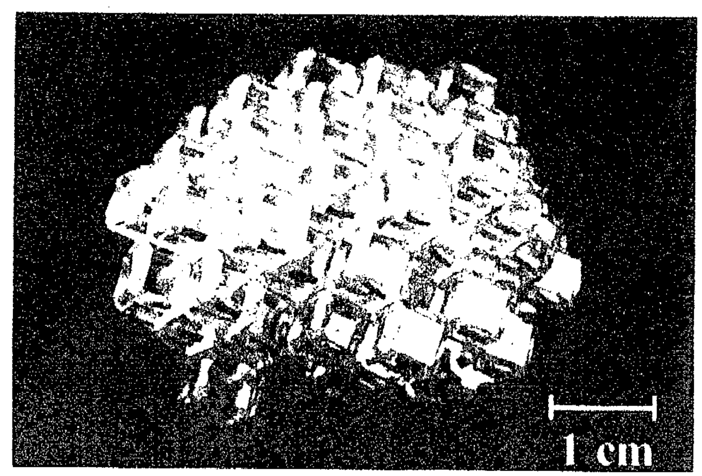
- To use self-assembly of patterned mesoscale objects to generate regular, 3D structures with open architectures

Technical Approach: Capillary Forces

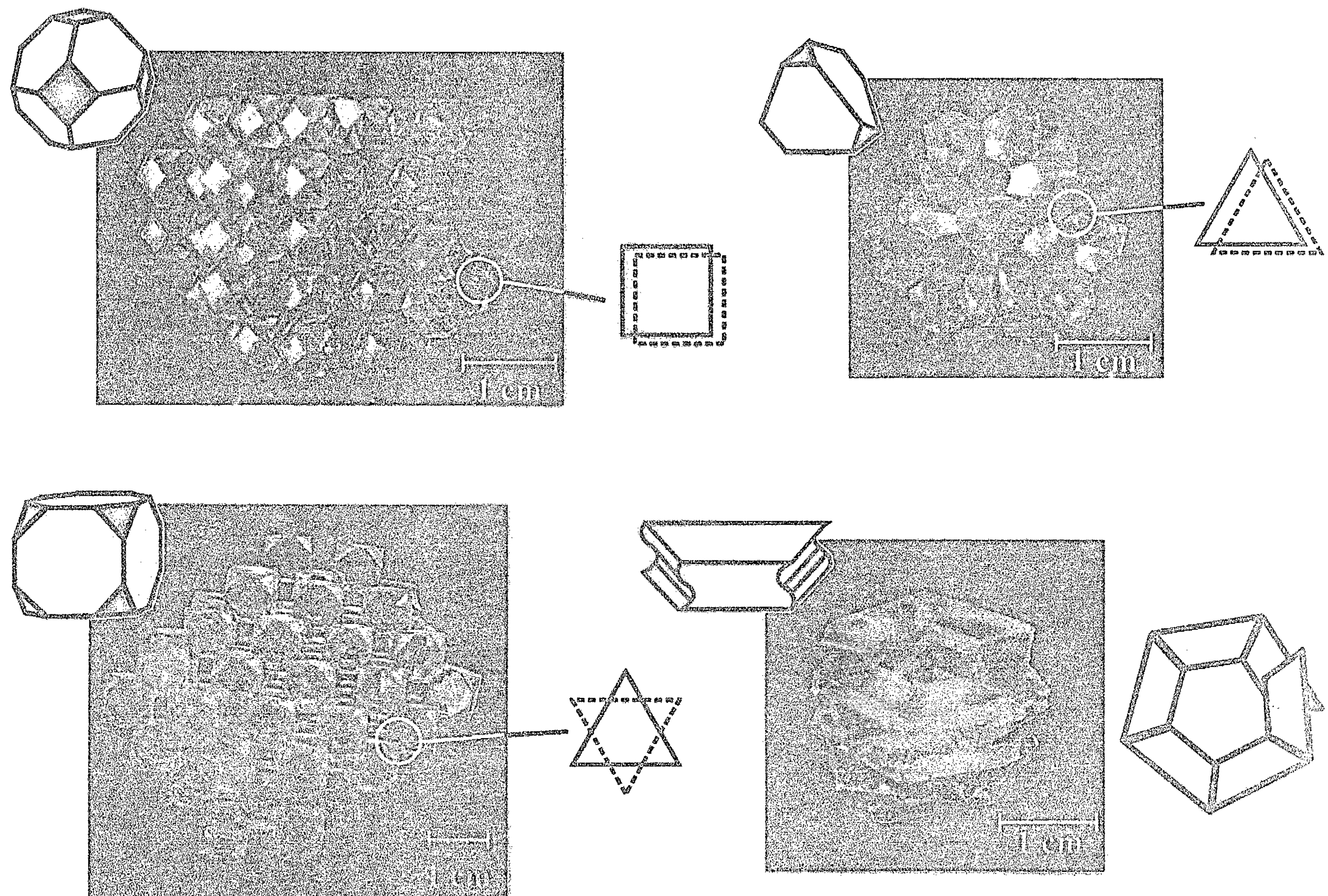


Accomplishments:

- Achieved control of self-assembled structures using alloy/aqueous KBr system
- Produced mechanically stable, free-standing structures after cooling
- Formed defect-free, extended lattices of 100 components



Self-Assembled, Open, 3D Lattice Mesostructures



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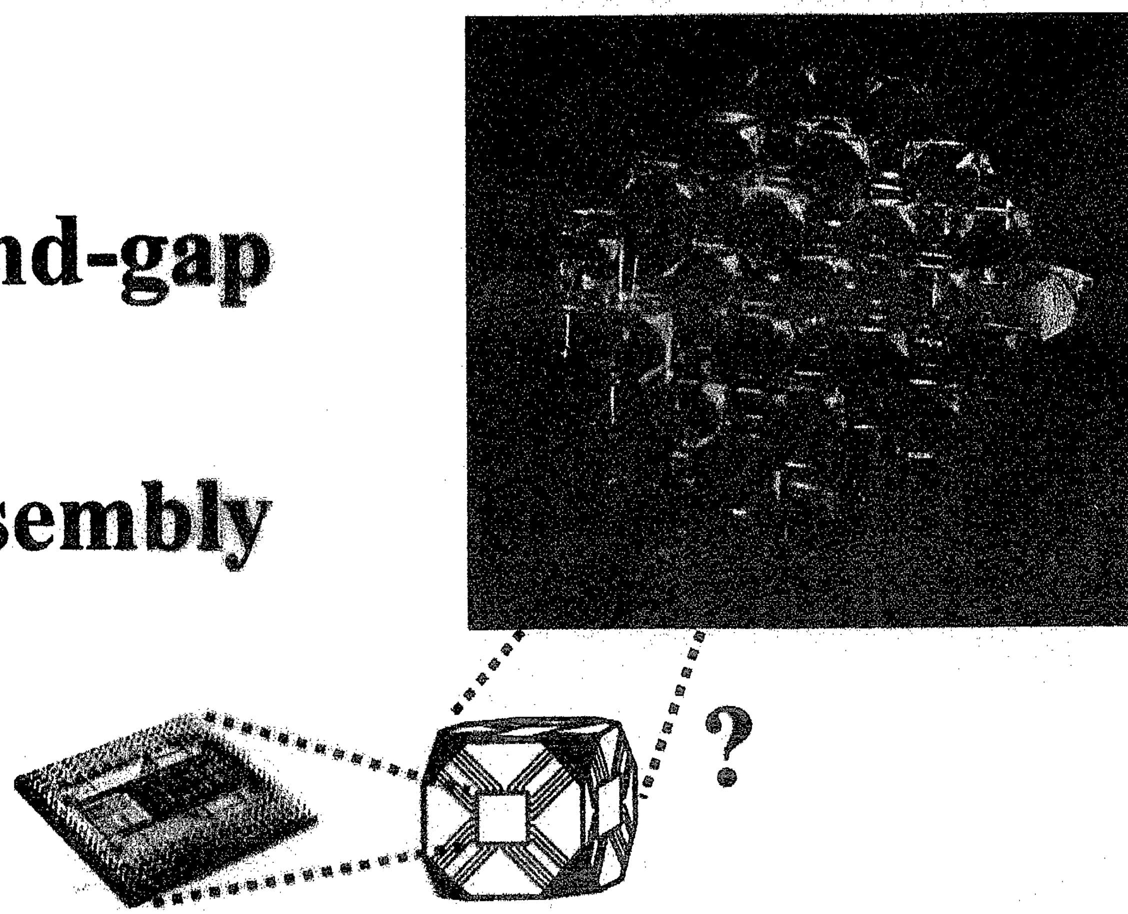
Applications

- 3D memory
- Photonic band-gap crystals
- Precision assembly



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An Increasingly Novel Technology for Microchemical Systems: ***Silicon Micromachining***

Martin A. Schmidt

Professor, Electrical Engineering and Computer Science

Director, Microsystems Technology Laboratories

Massachusetts Institute of Technology

Cambridge, MA USA

(617) 253-7817, fax:(617) 253-5228, schmidt@mtl.mit.edu

Alternate Titles:

- 'I'm not dead yet'
- 'The rumors of my demise are greatly exaggerated'
- 'Watch out David, Goliath still has a pulse'

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What's Wrong With Silicon?

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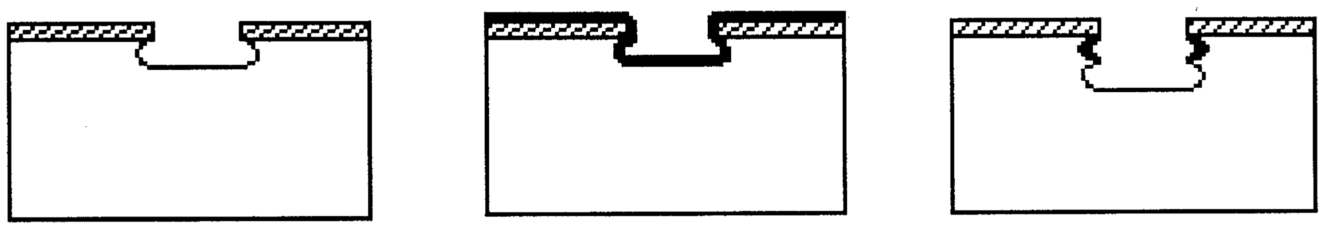
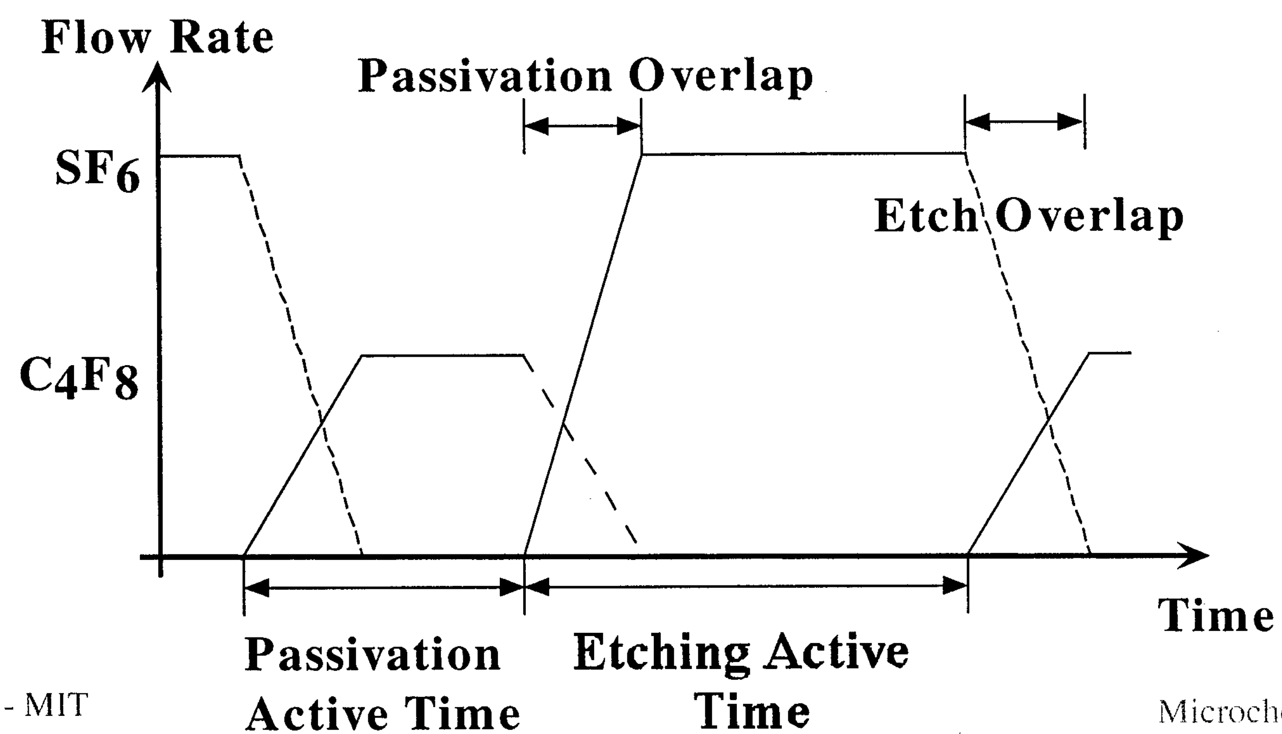
- Access to the technology (capital intensive)
- Manufacturing favors high wafer volumes
  - ~10,000 wafers/month
- Fundamentally open loop manufacturing
  - Run-by-run control
- Cumbersome IC industry protocols
  - Cycle time
- Cost of material and process

Why Use Silicon?

- Excellent material
  - High strength
  - No creep
  - High temperature capability (~600C)
  - Electronic properties
- Tremendous material and process knowledge base
  - Precision
- Large and reliable support infrastructure

DRIE Process





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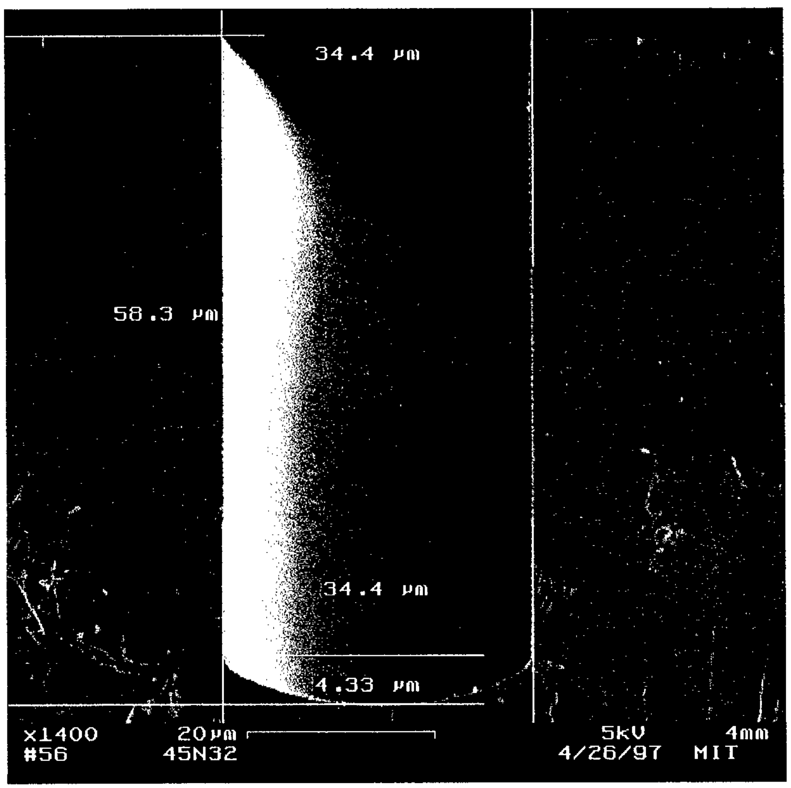
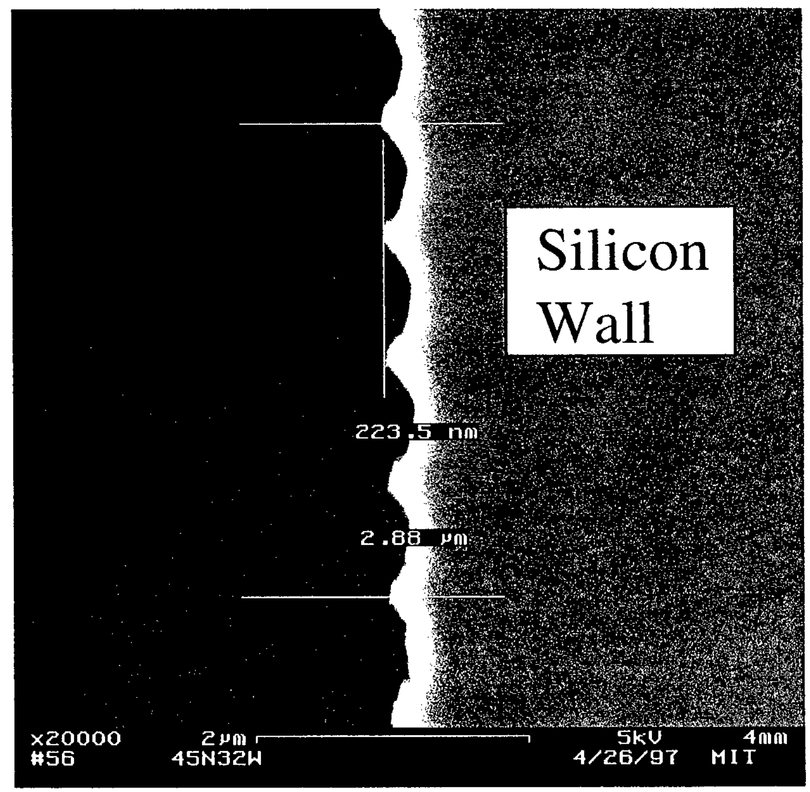
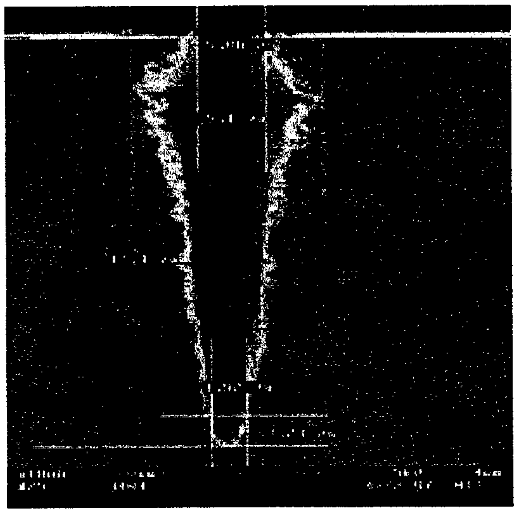
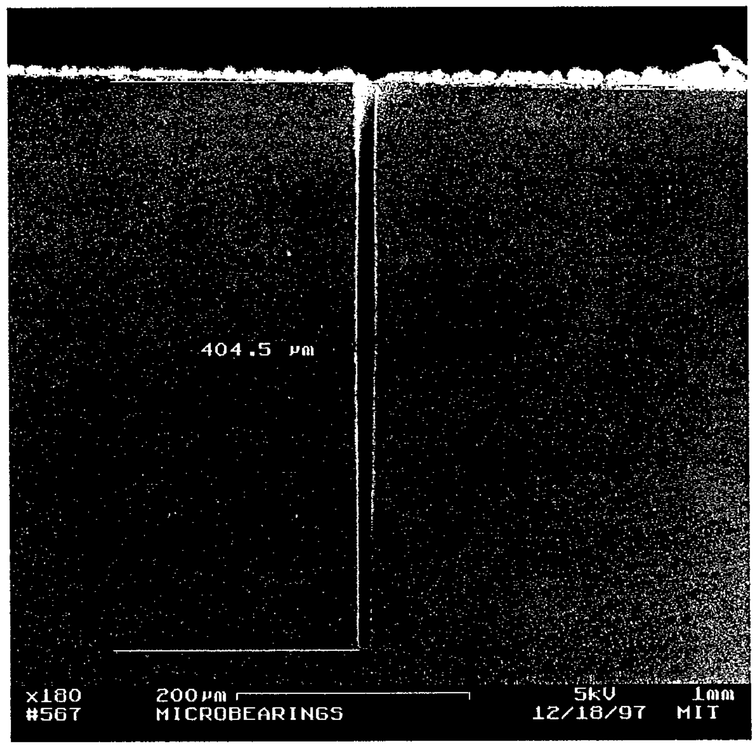
DRIE Example

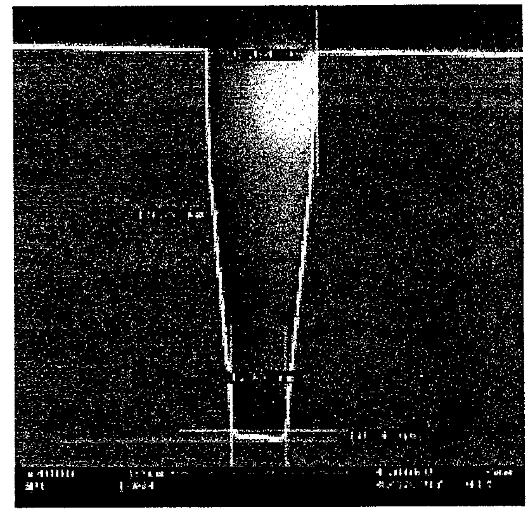


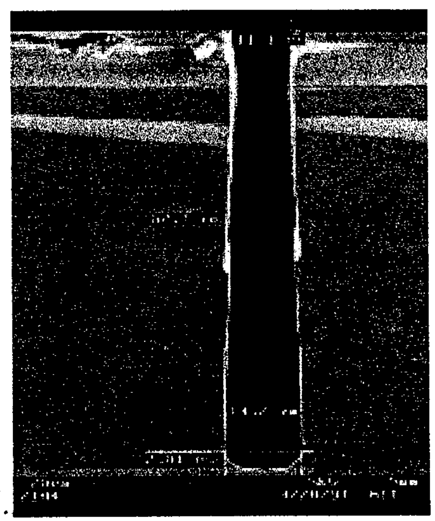


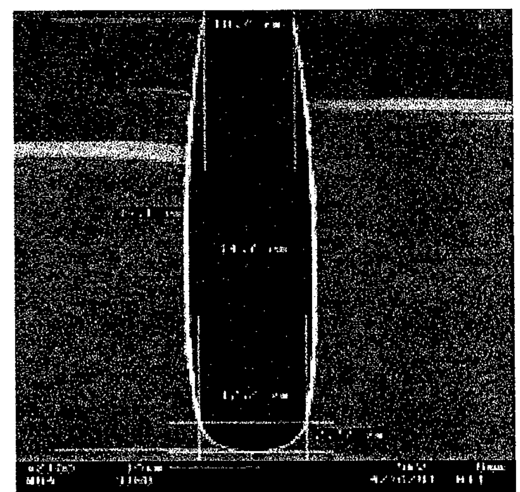
Examples of Etch Profiles











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Parameter Space

Etching Cycle:	**Passivating Cycle:**
SF_6 Flow Rate	C_4F_8 Flow Rate
Electrode Power	Electrode Power
Active Cycle Duration	Cycle Cycle Duration
Cycle Overlap	Cycle Overlap
Coil Power	Coil Power

Pressure ⇔ Automatic Pressure Control Valve

Etch characterization uses a resist mask (6-10 micron thick)

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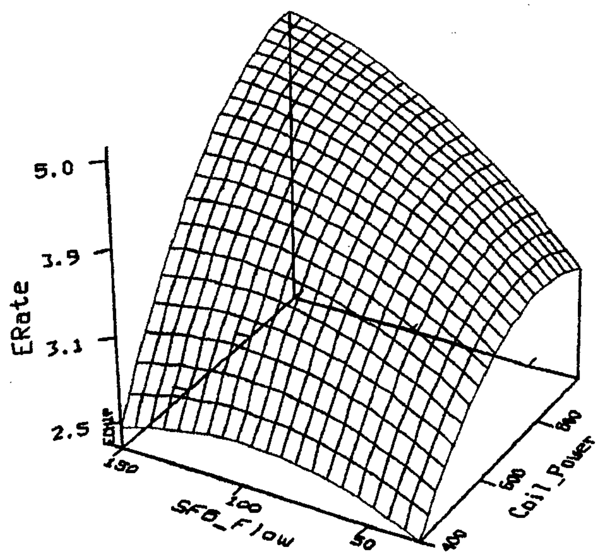
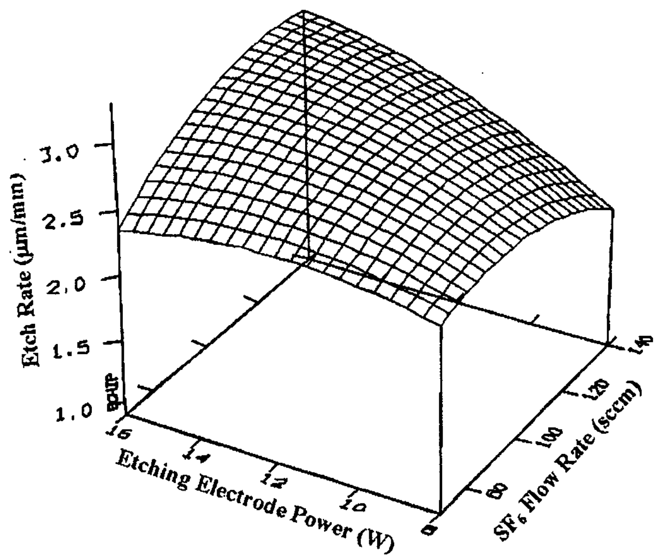
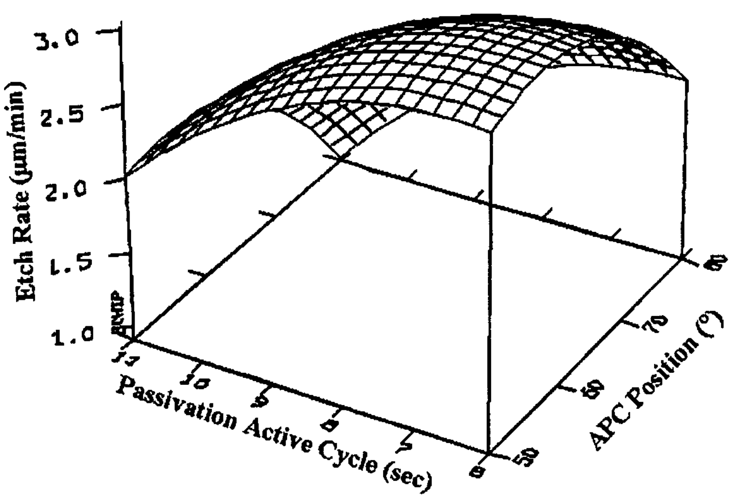
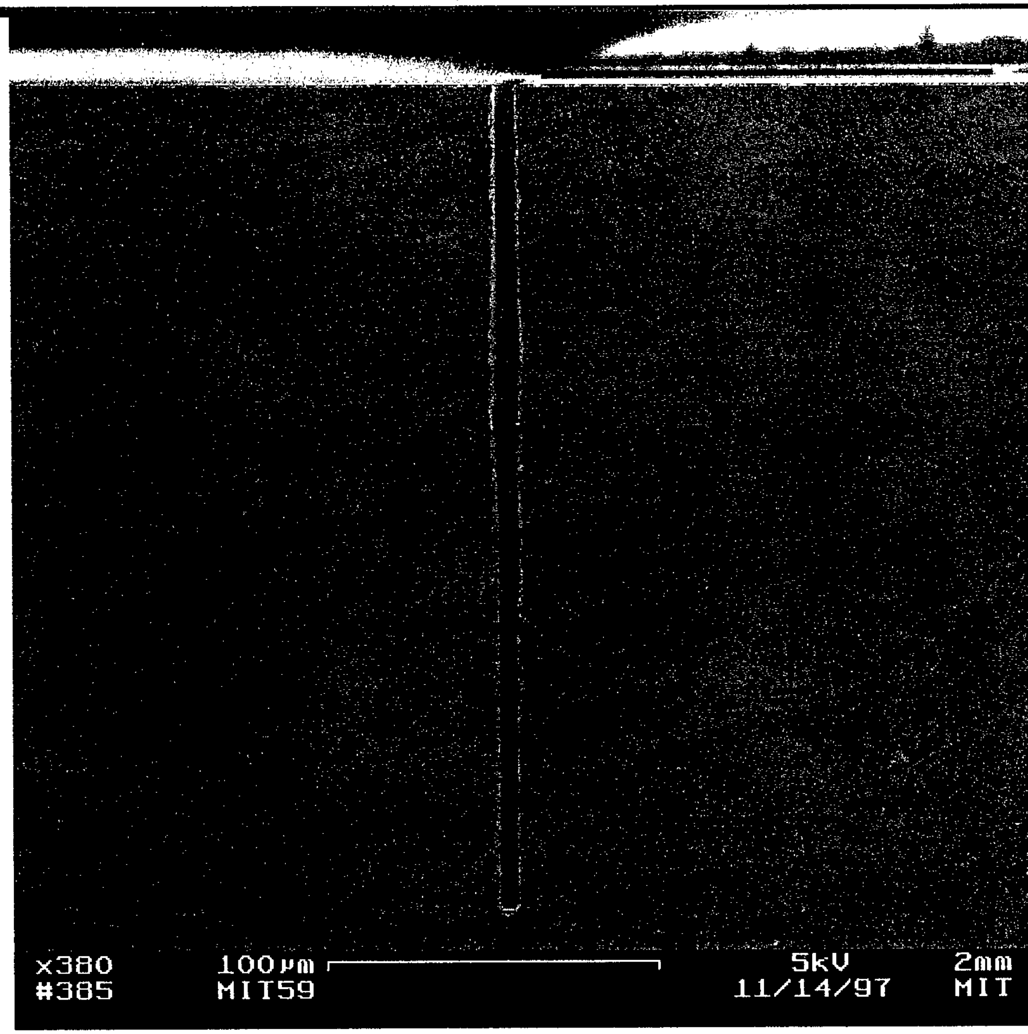
Silicon Etching Rate



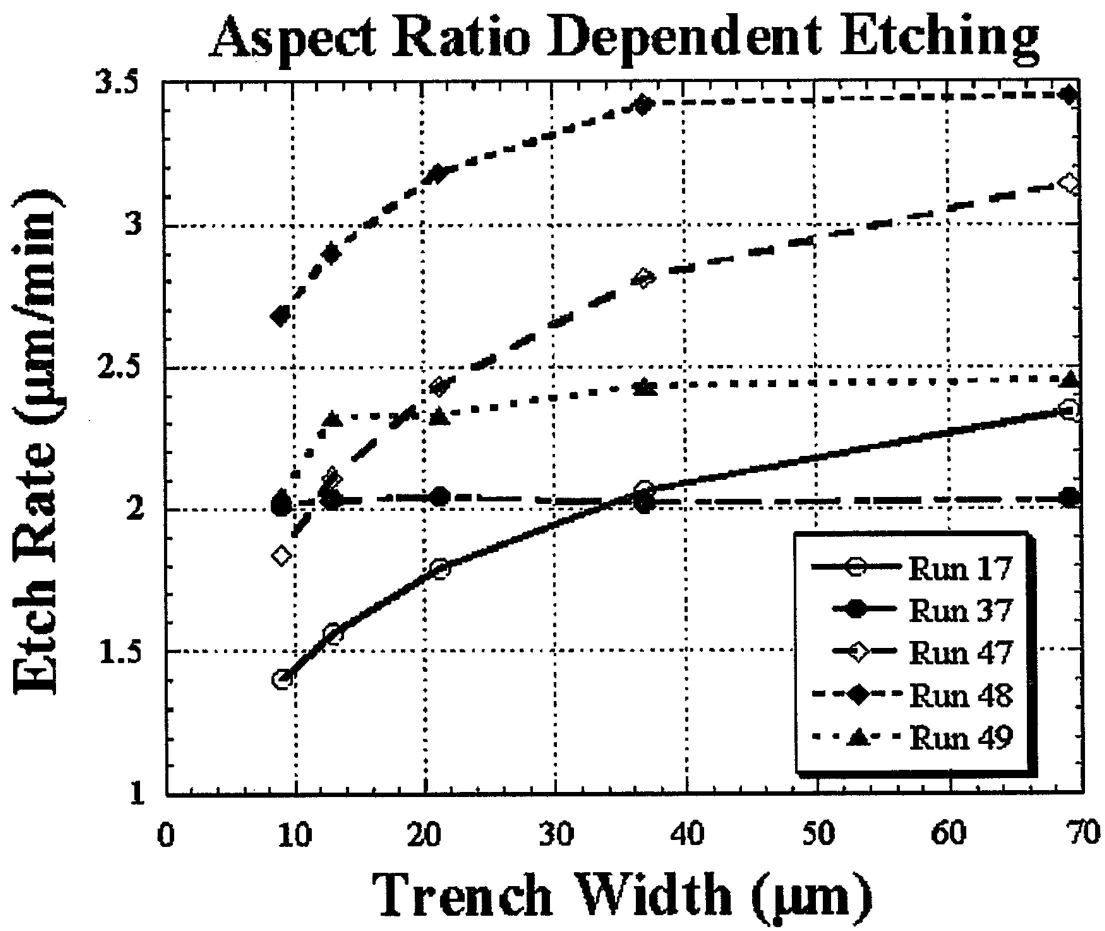




Optimized 400 μm Bearing Etch



Aspect Ratio Dependent Etch



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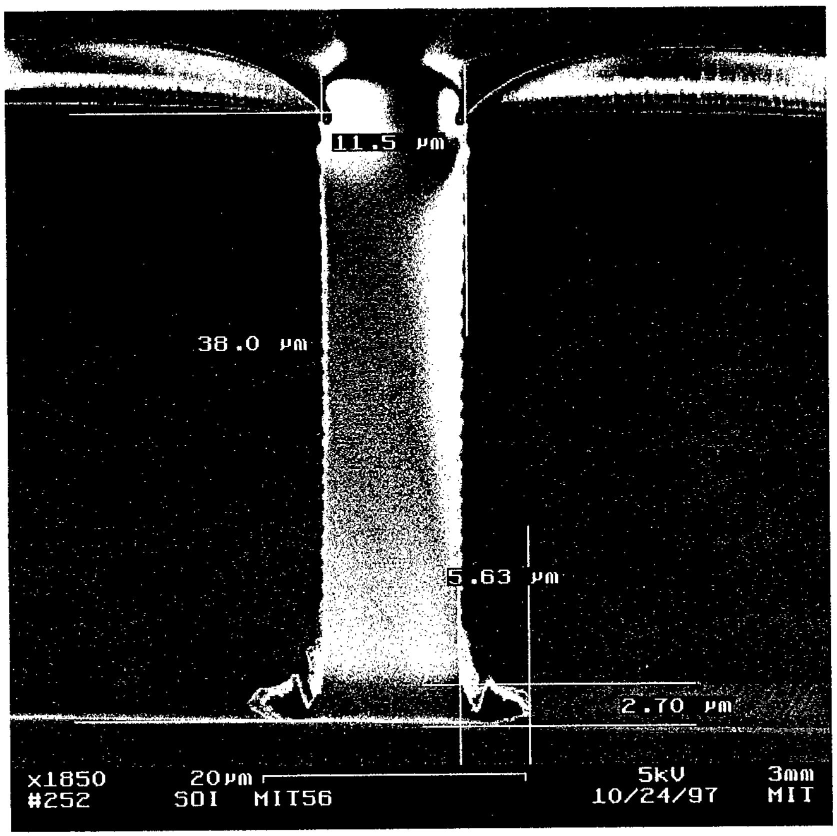
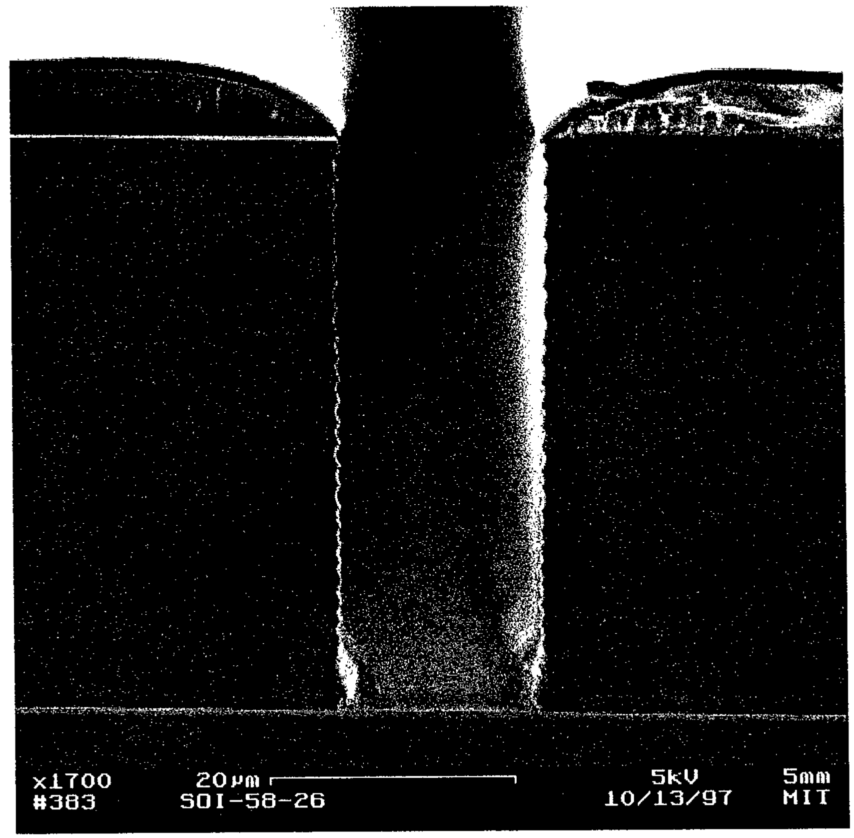
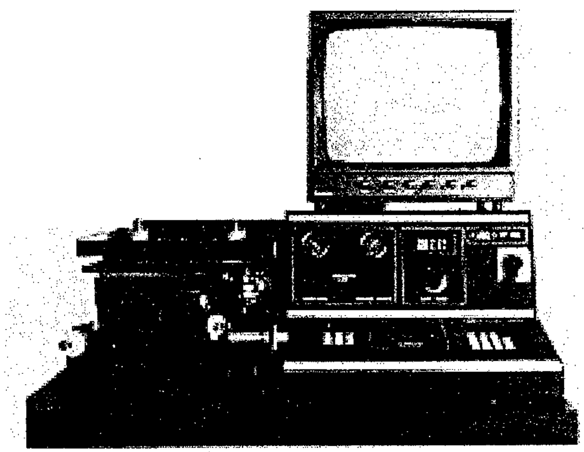
Footing Effect



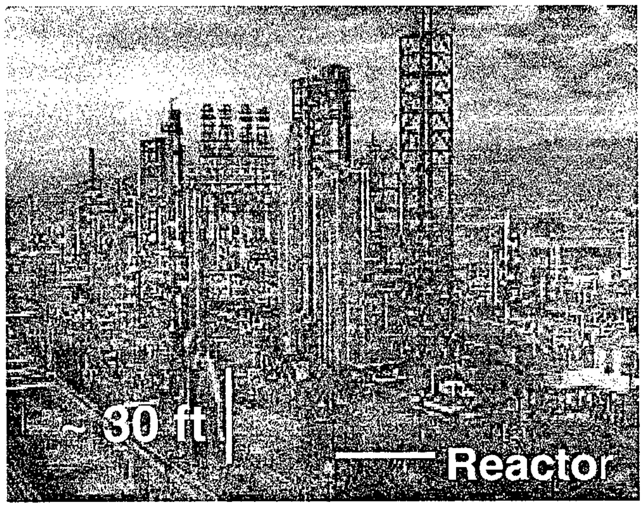


Aligned Wafer Bonding

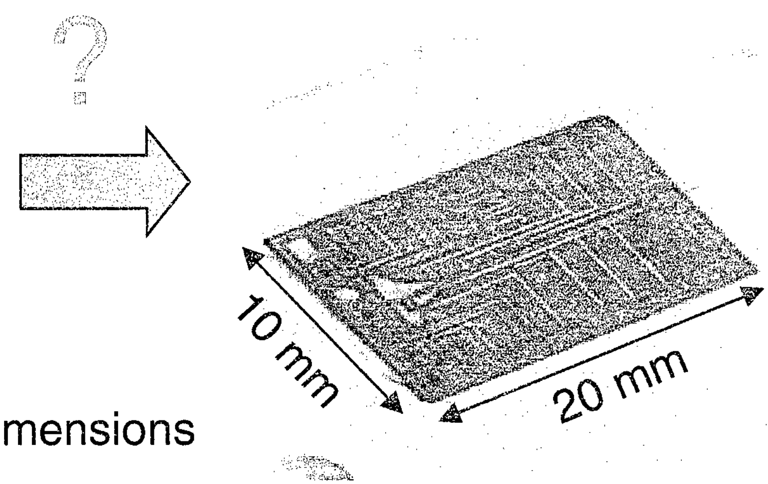


- Commercial tools exist
- Permits multi-wafer stacks
- 2 micron alignment spec
- Pressure head on the bonder is critical
  - Suppress bow of thick wafers
- Typical bond temperature
  - ~1000C

Microchemical Systems - Motivation

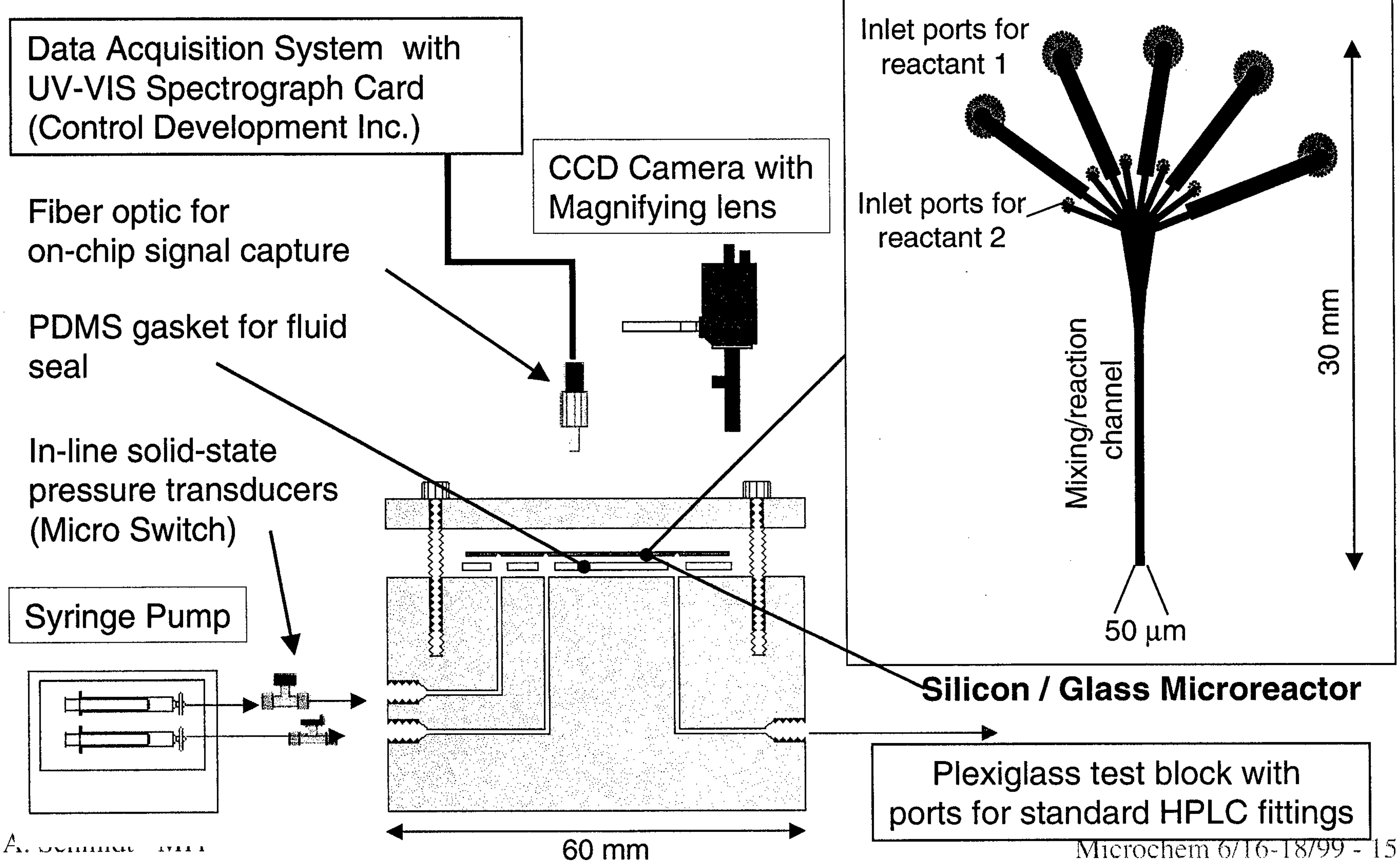


- Can scale-up by replication of microfabricated reactors as opposed to a few large units revolutionize chemical production?

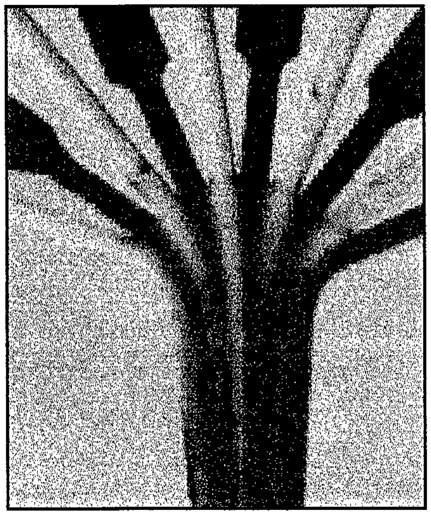


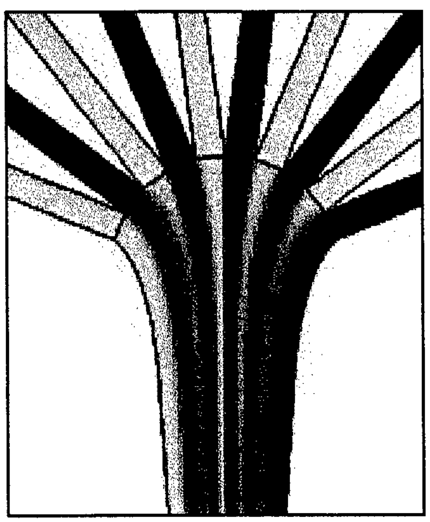
- Potential advantages:
  - Safer operation in small dimensions
  - Improved chemical performance
  - Distributed manufacturing - on demand production of toxic intermediates
  - Fast scale-up to production by replication
  - High throughput reaction/catalyst screening - combinatorial chemistry

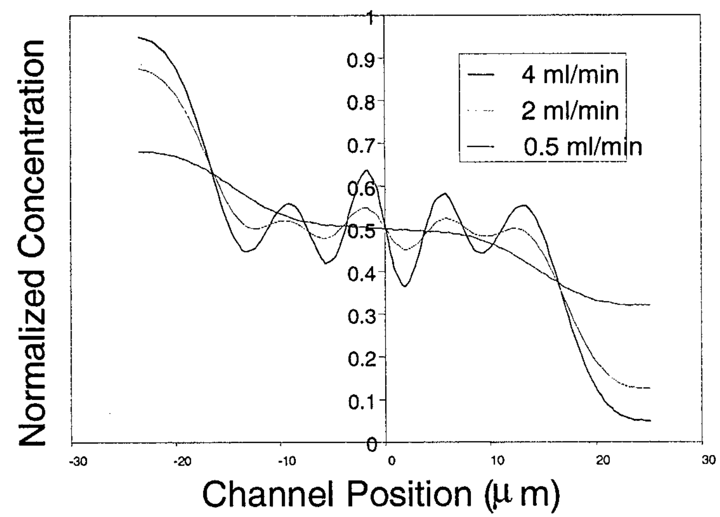
Liquid Phase Microreactor



Experimental And Modeling Results

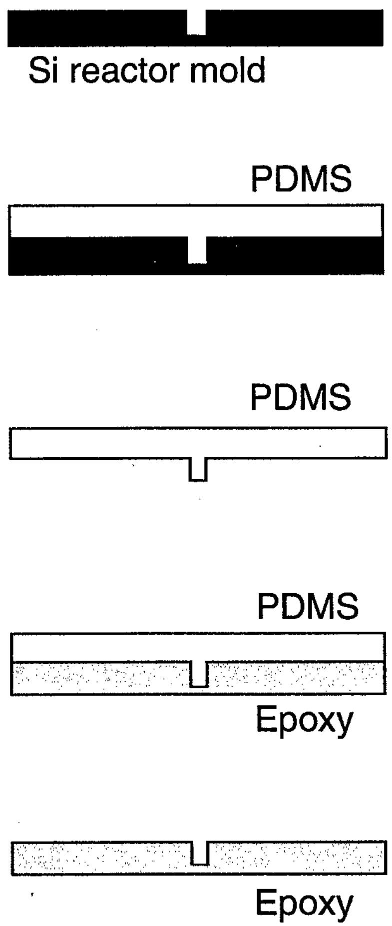


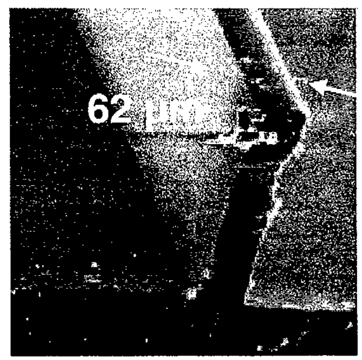




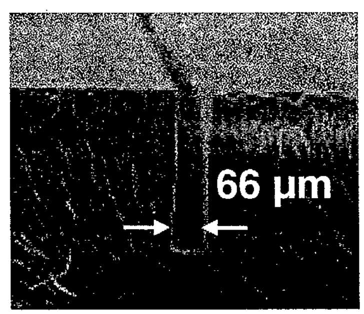
Concentration Profiles at Varying Flow Rates

Micromolding Liquid Phase Reactors

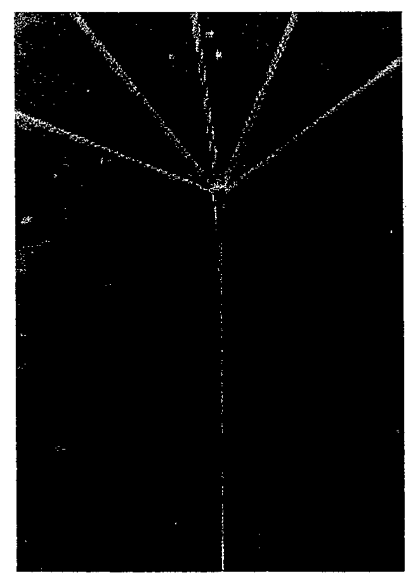




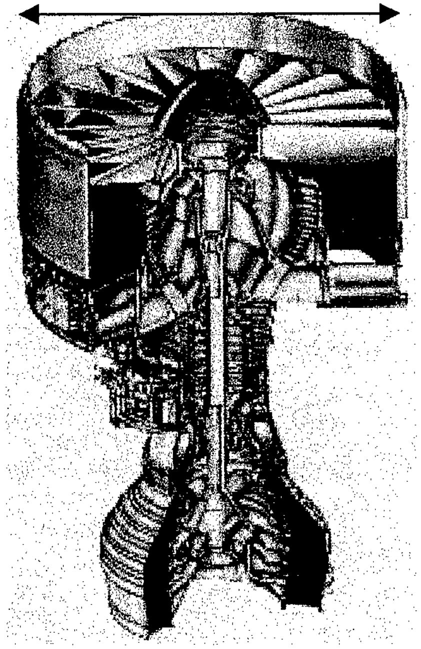
PDMS mold

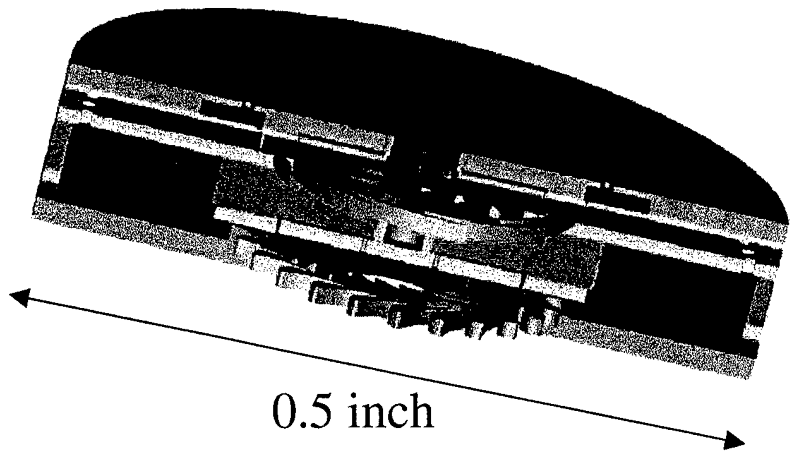


Epoxy reactor



MIT Micro Gas Turbine Generator





	Micro Turbo Generator	LiSO2 Battery (BA5590)
Power Output	50 W	50 W
Weight	50 grams	1000 grams
Specific Energy	3500 W-hr/kg	175 W-hr/kg

– A portable power source with ten times the power density of state-of-art batteries

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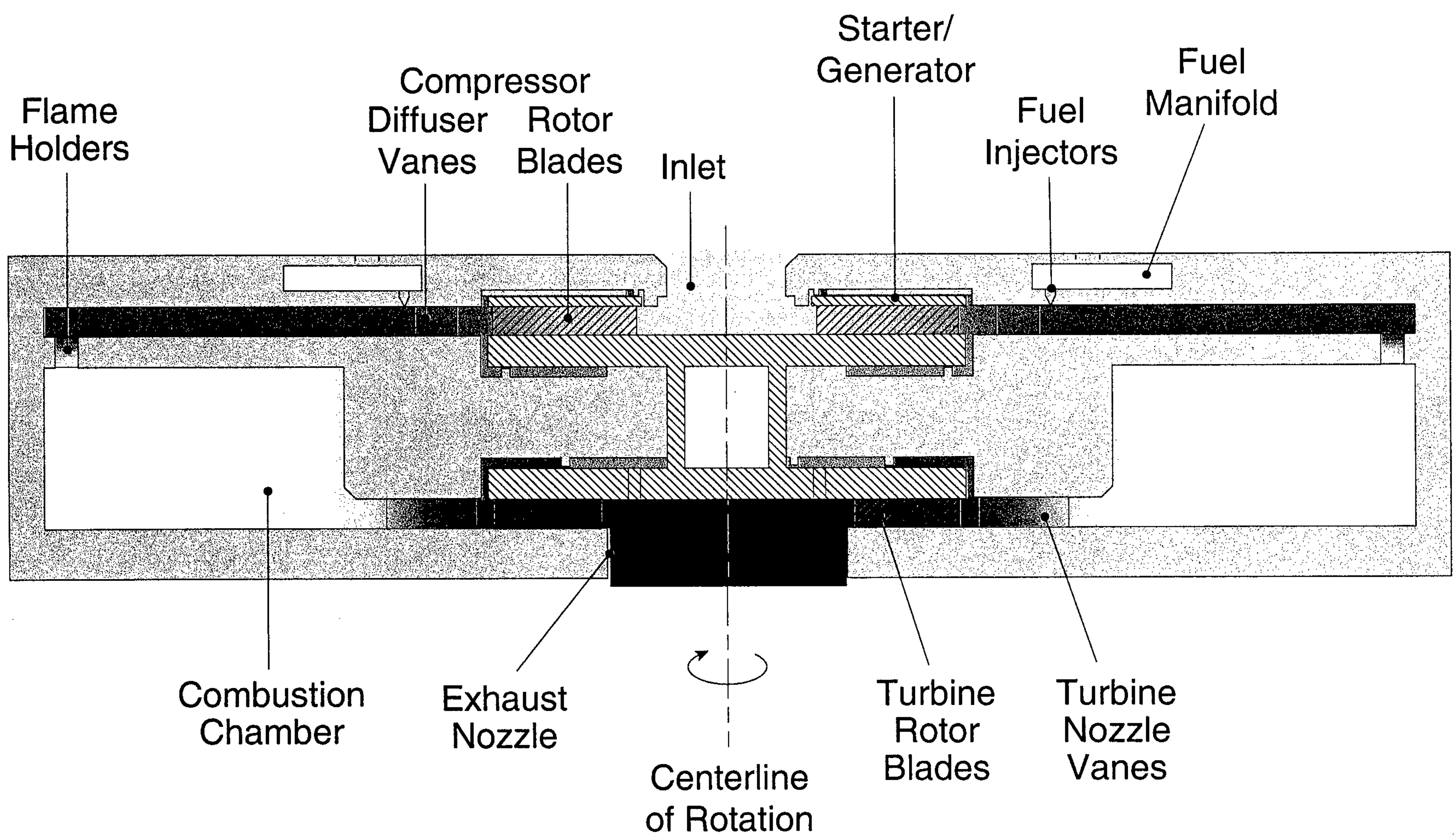
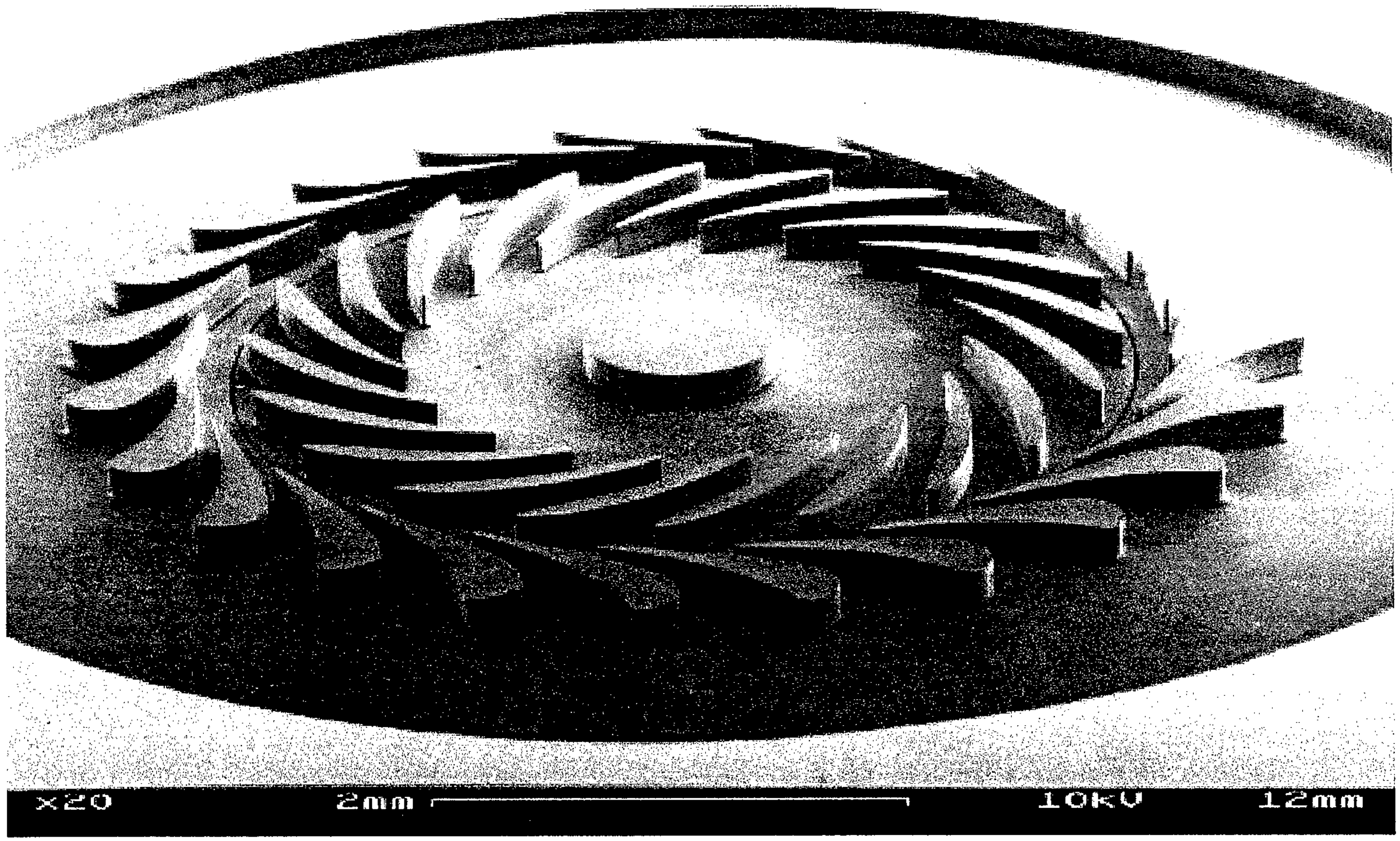
How do you build it?

- Constrain design to extruded 2-D shapes
- Achieve 3-D by lamination of wafers
  - Aligned bonding
  - *Yield statistics benefit*
- Utilize laser assisted etch to 'release' captured parts

MIT Microengine



Microturbine Rotor



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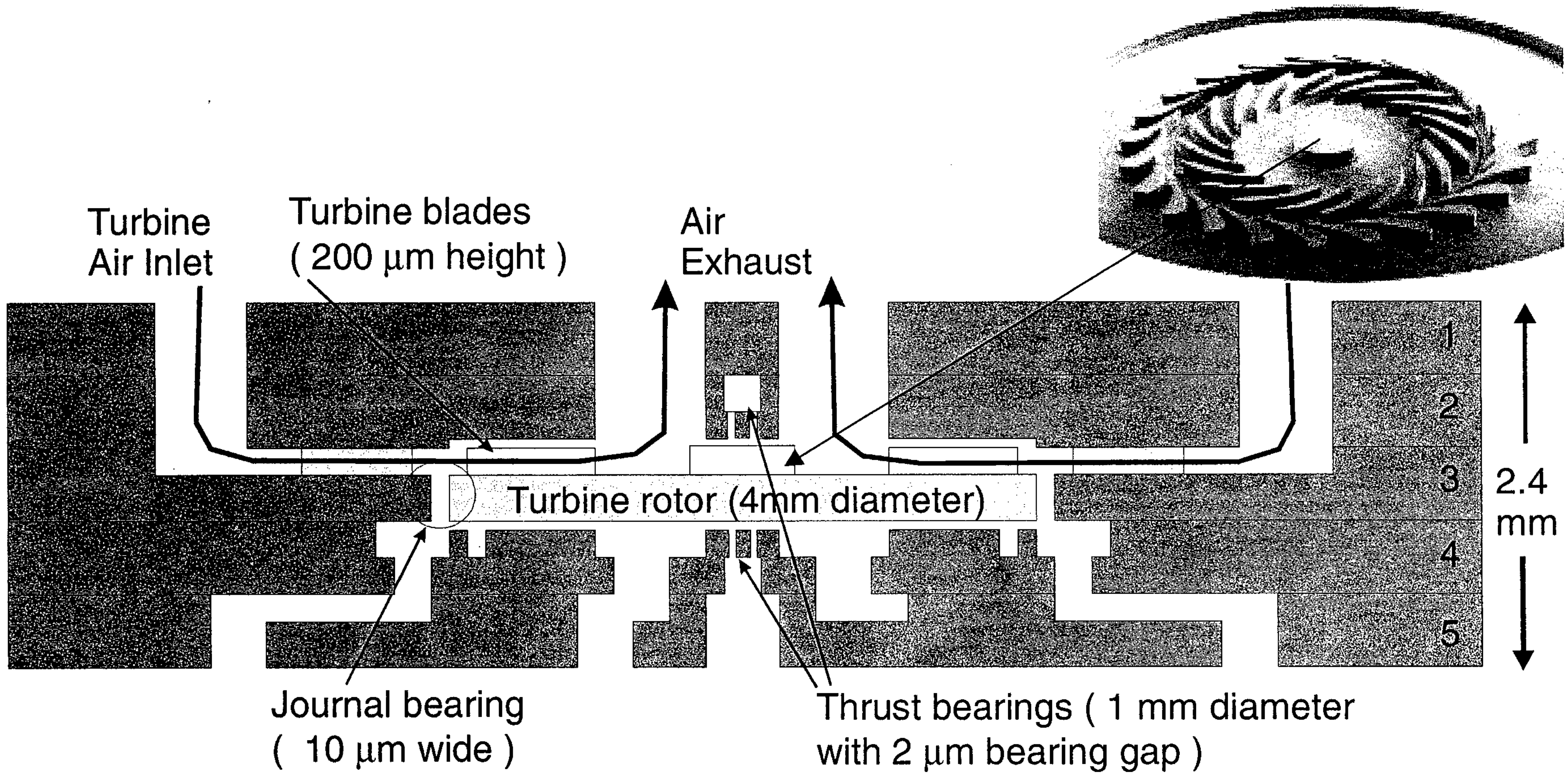
Micro Bearing Rig Layout



Microbearing Rig

Wafer

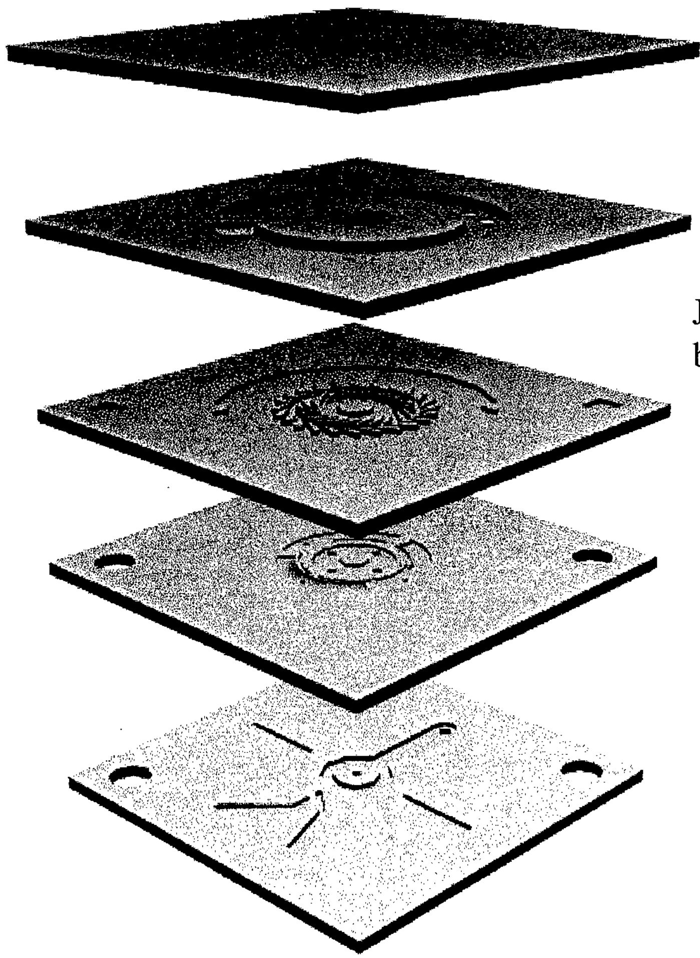
1

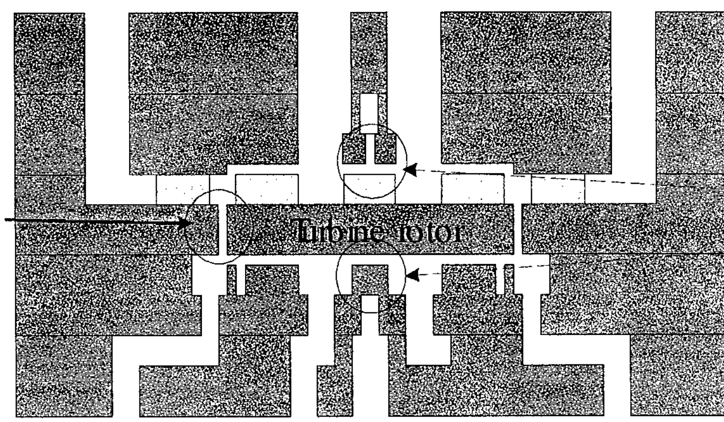
2

3

4

5





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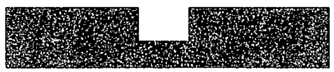
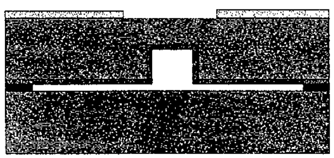
Fabrication Challenges

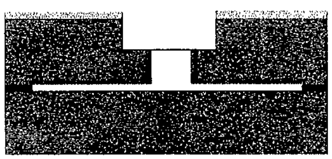
- Aligned through-wafer DRIE
  - aspect ratio > 30:1 , > 300 μm deep etch
  - trench profile and fillet radius control
- Aligned multiple-wafer fusion bonding
- Create free-standing moving parts
  - laser assisted etch (LAE) of silicon
- Critical dimension control

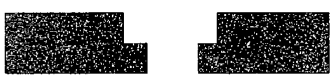
Multiple Aligned Through-Wafer Etching /Bonding Protocol

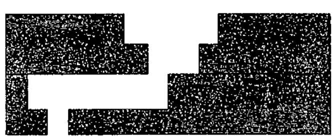

Front side DRIE


Deposit front side sacrificial protection layer


IR wafer front to back aligned patterning
Reversible handle wafer attachment


Back side DRIE


Handle wafer separation, wafer cleaning


Aligned wafer to wafer fusion bonding

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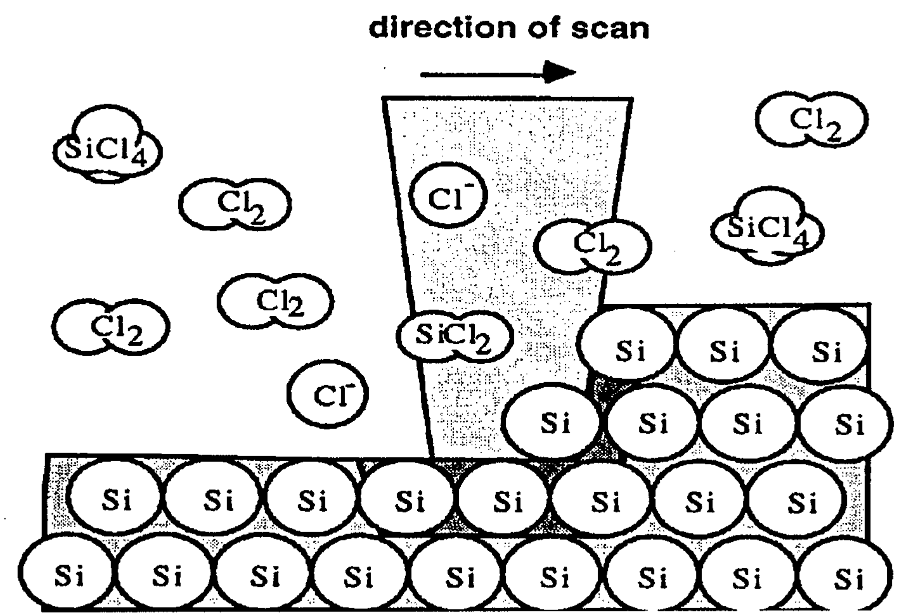
Laser Assisted Silicon Etch

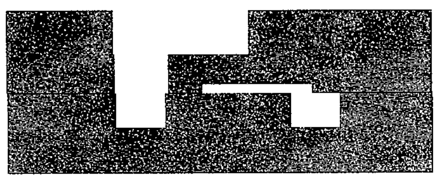
- Argon Ion Laser (8W)
- Etch rate ~ $10^5\ \mu m^3/min$



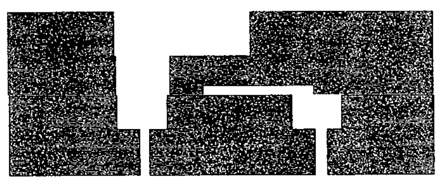
Ref: T. Bloomstein (1996)

Create Free-Moving Part - Sacrificial Tab Etch

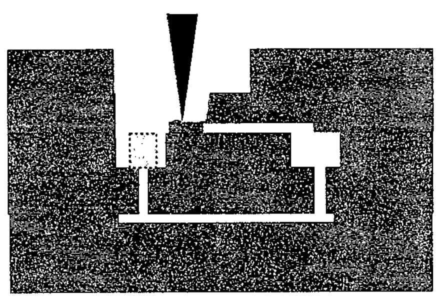
1st deep etch halfway through the wafer



Bond to another wafer that has sacrificial tab



Perform 2nd deep etch, sacrificial tab holds the free part



Bond to third wafer

Laser assisted etch removing the tab and release the free-moving part

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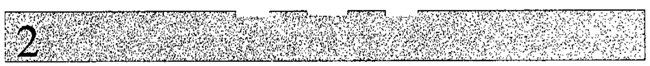
Process Flow - 1

- fusion bonded 5 wafer stacks, 16 masks, and 9 deep RIE

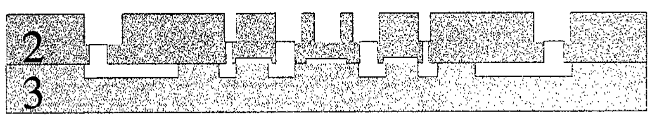


Patterning bearing gap and tip clearance through plasma etch (2nd wafer)

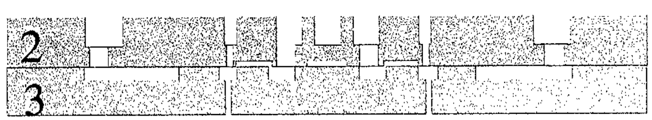
1st aligned deep RIE to define flow channels

2nd deep RIE to define bearing restrictors

Deep etch rotor blades on 3rd wafer



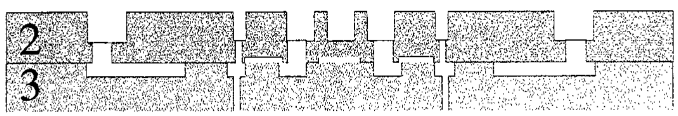
Aligned fusion bond 2nd and 3rd wafer



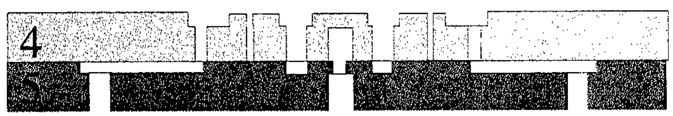
Journal bearing patterning and etch

Process Flow - 2

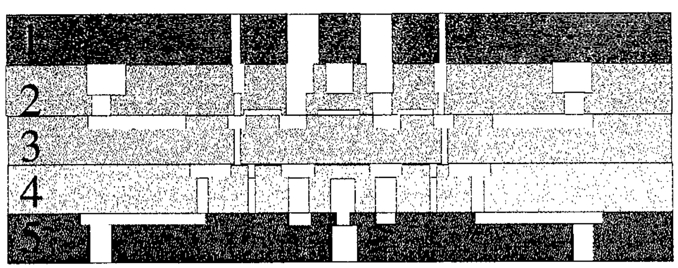
Through wafer etch to define 1st wafer



Bonded 2nd and 3rd wafer

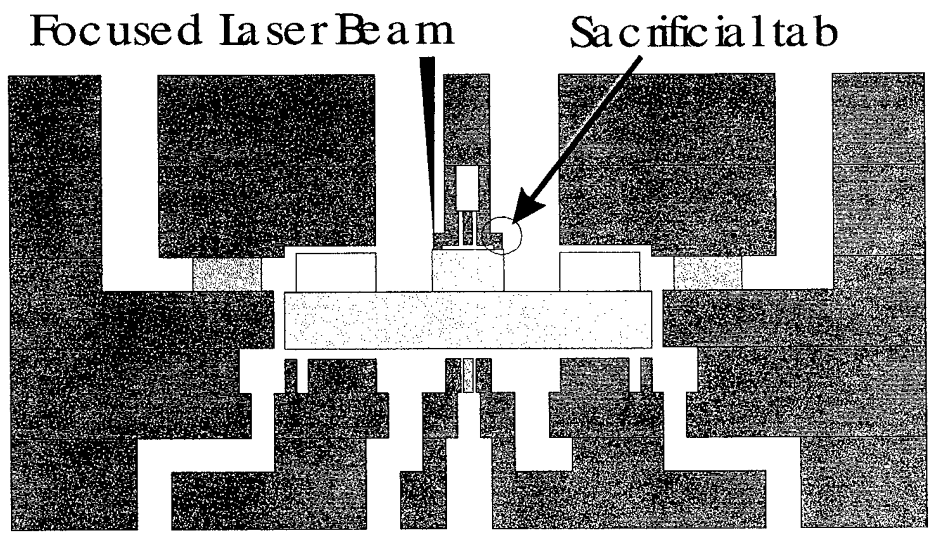


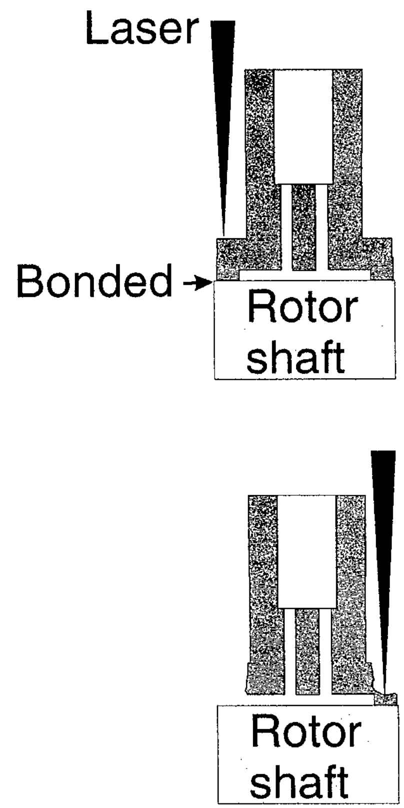
Bonded 4th and 5th wafer



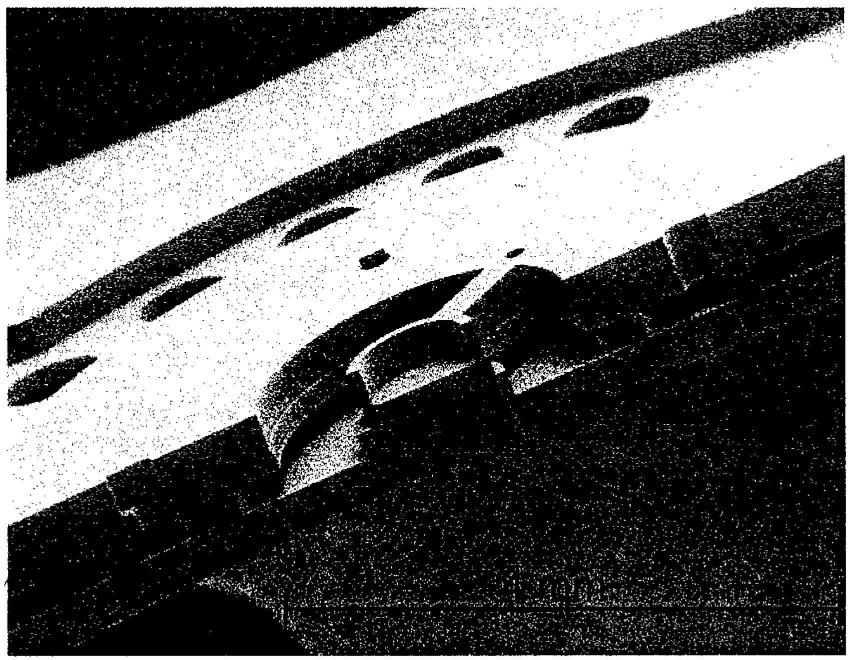
Aligned fusion bond 2/3 to 4/5, then to 1.
Die separation.
Laser assisted rotor release etch.

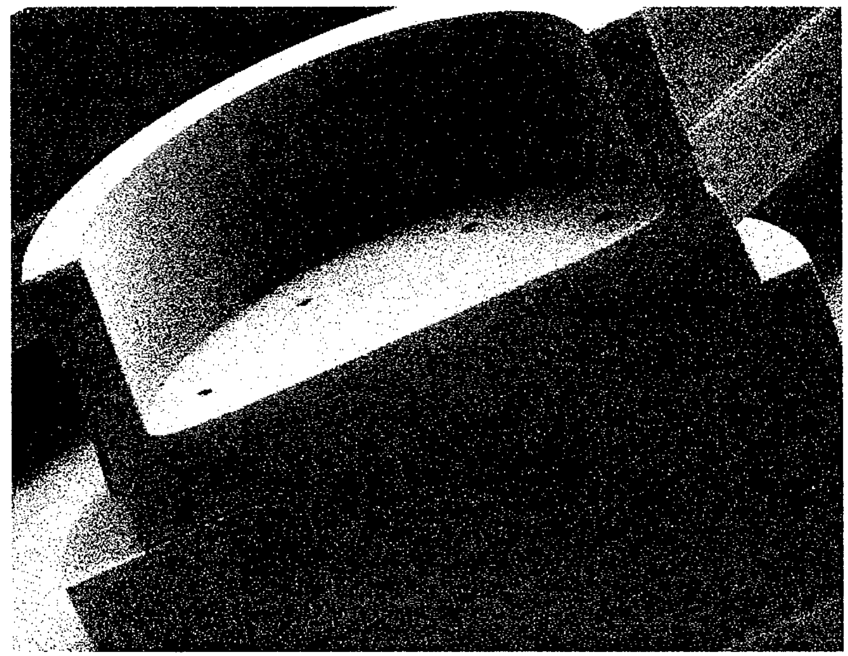
Laser Assisted Rotor Release



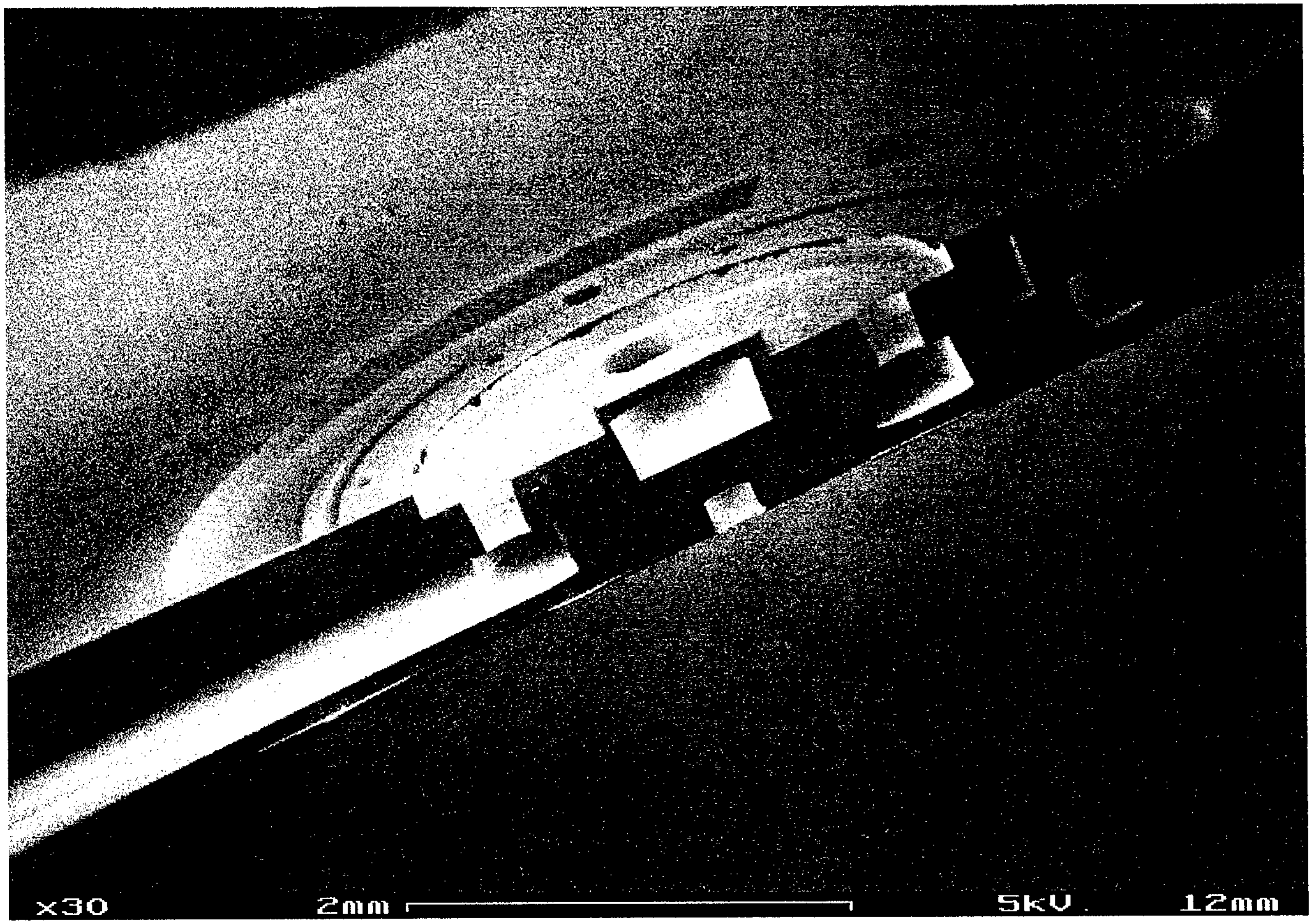


Bonded 2nd/3rd Wafer Pair





Bonded 4th/5th Wafer Pair



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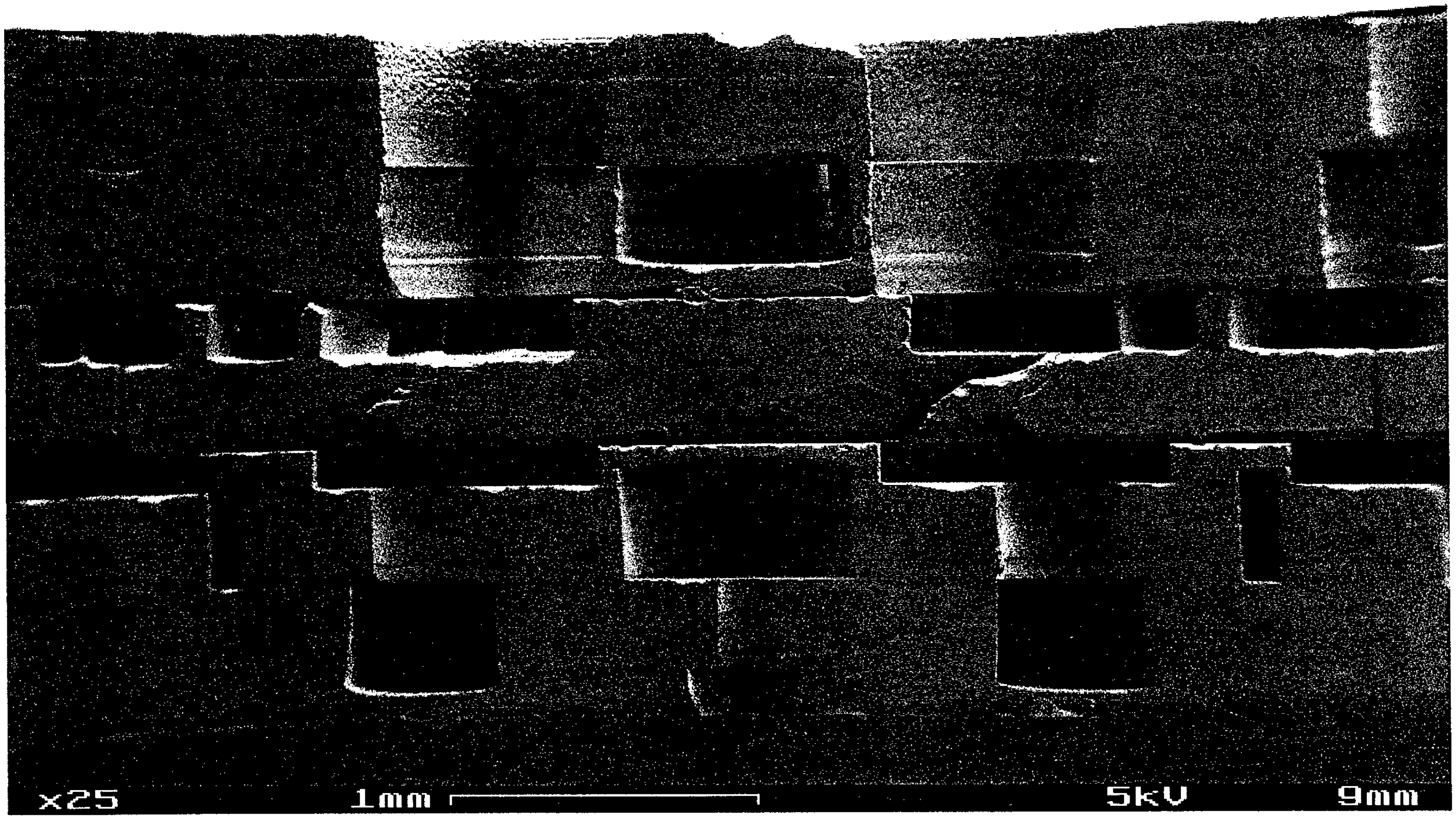
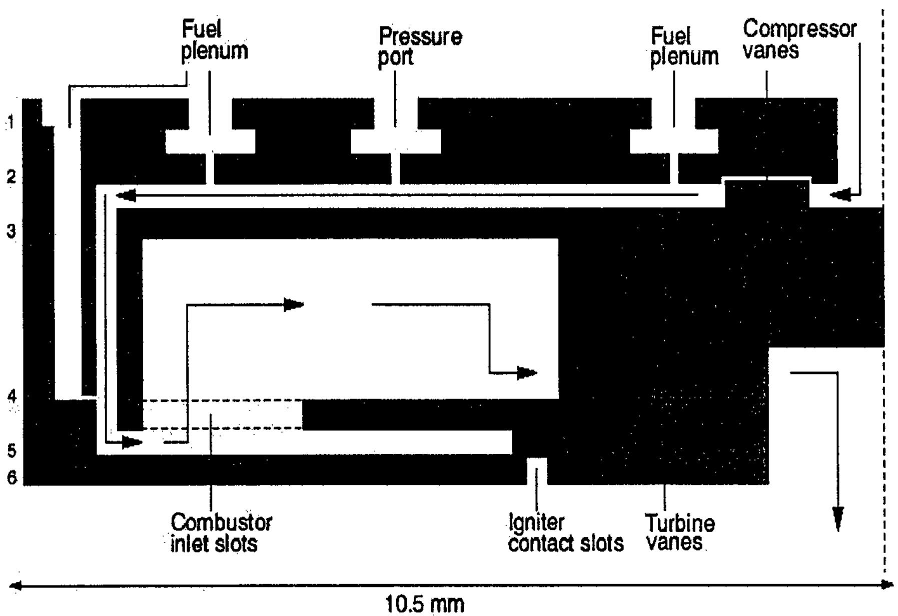
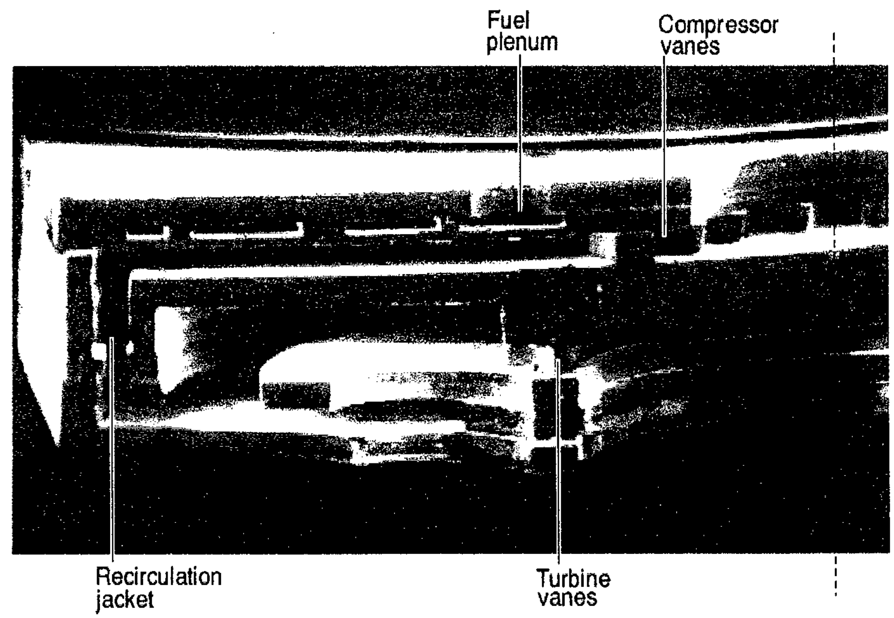
Microbearing Rig



Six-Wafer Microcombustor





15 masks, 12 deep etches through 3.8mm, 5 aligned wafer bonds

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Technology Lessons Learned

- DRIE + Wafer Bonding
  - An interesting 'prototyping' technology
- DRIE
  - Breaks the IC manufacturing paradigm
    - » wafers/hour ➡ hours/wafer
  - $1/micron cost of ownership
  - Expect to see ~10x reduction in this cost
    - » Equipment vendors change from IC equipment manufacturing model to machine tool model
    - » Increased throughput

Product Lessons Learned

- Three most important things in Power MEMS
  - precision, precision, and precision
- Fab cycle time paces design
- Need for robust technology models
- Higher temperature materials can add value
  - SiC molding

A Silicon Microsystems/MEMS Editorial

- Packaging
  - Integrate package function
- Focus on the enabling elements:
  - Small Size / Low Power Consumption
  - Monolithic Integration of Arrays
  - Monolithic Integration with Electronics
  - Batch Fabrication
- Avoid
  - Cost justifications
  - Analogies to the IC industry

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Integrated Micro-fluidic Systems Fabricated in Low Temperature Co-fired Ceramic Tapes

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Post Docs & Students

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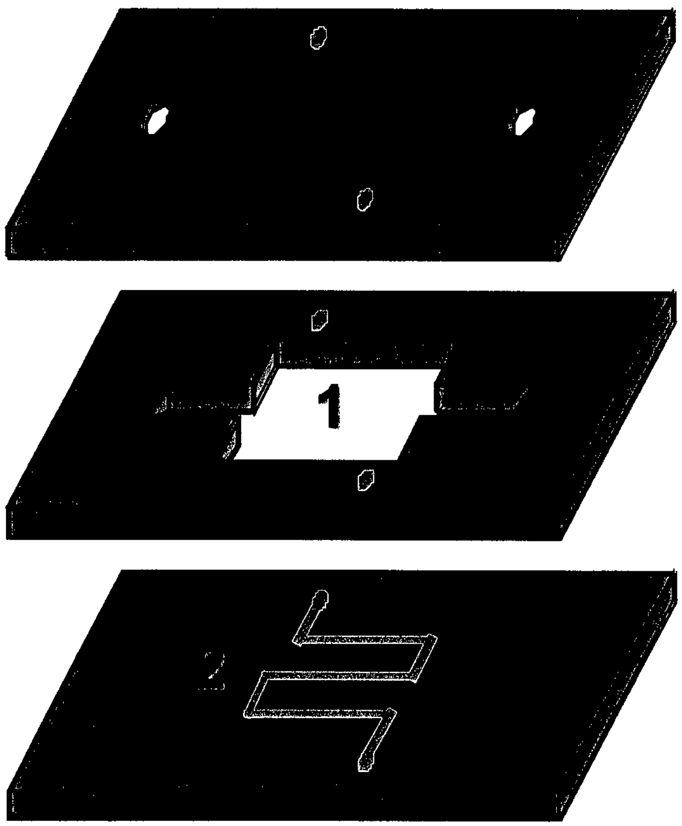
Support

DARPA Grant N66001-97-1-8911

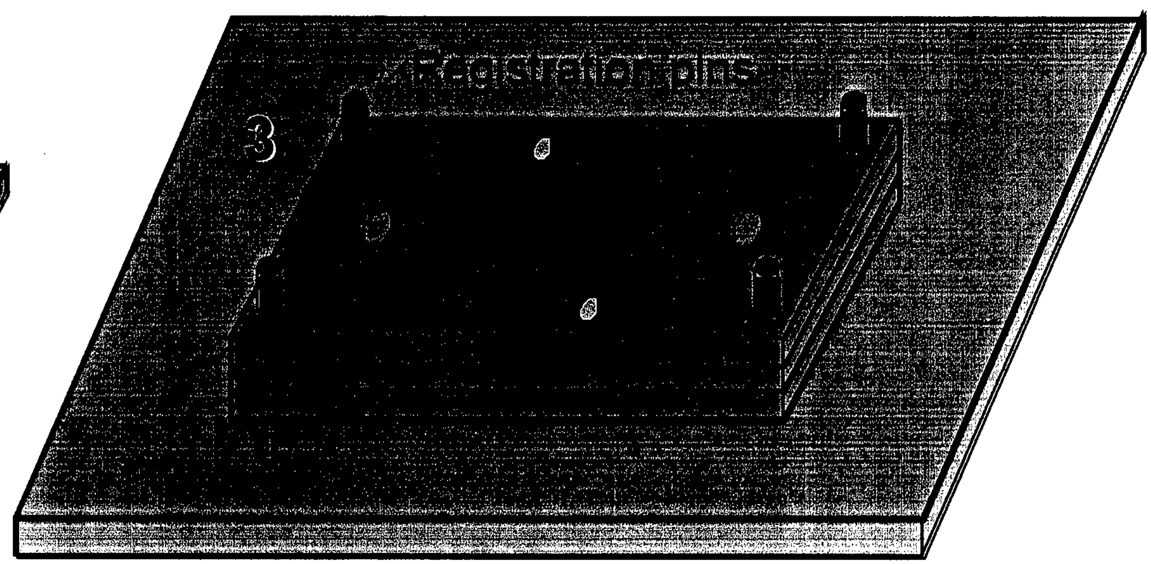
Flexible Layered Manufacturing of Meso-scale Systems Using Ceramic Tapes



1. Machining each layer to create desired patterns

2. Screen-printing and via filling or thin film deposition through a mask

3. Alignment and Stacking



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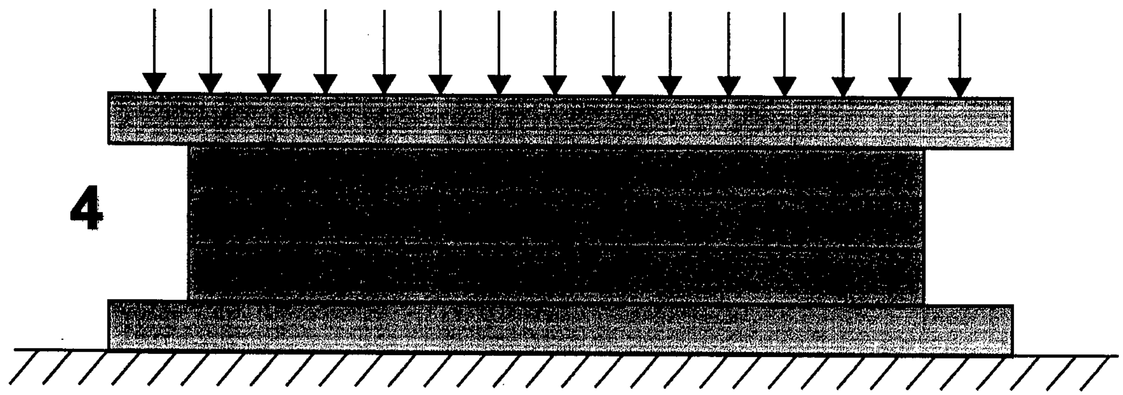
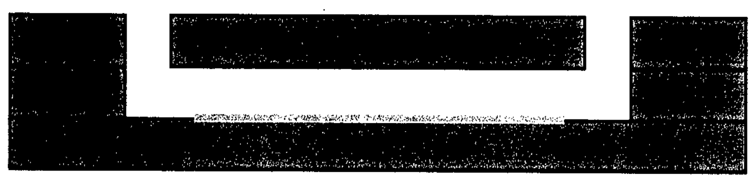
Flexible Layered Manufacturing of Meso-scale Systems Using Ceramic Tapes

4. Lamination

Lamination pressure of 3000 psi



5. Co-firing



Cross-section after firing

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Highlights of Ceramic Tapes for Integrated Mesoscopic Systems

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- **Easily Machinable:** In the green state, ceramic tapes are soft, pliable, and easily machinable. The material facilitates easy fabrication of mesoscopic features (10μm - 10mm). In the fired state, small and <u>precise</u> structures can be machined using diamond tools, abrasive jets, and/or lasers.
- **Tailored Properties:** It is possible to cast tapes of various ceramic compositions to obtain desirable properties. Thus, desired properties such as low/high thermal conductivity, and piezoelectric and magnetic layers can be obtained.
- **Laminated 3-D Structures:** Large number of layers can be laminated to form three-dimensional structures.
- **Easy Integration of Electronics:** A well developed thick film technology facilitates the deposition of various metals and electrical components on the tapes in the pre-fired state and the formation of three-dimensional interconnects. For example, one can embed conductors, electrodes, resistors, and thermistors.
- **Hybrid structures:** It is possible to fabricate hybrid structures consisting of ceramics, silicon, metals and/or some other suitable materials.

Highlights (continued)

- **High temperature operation is feasible**
- **Easy Packaging & Cost Advantage:** Packaging is difficult and expensive in silicon based MEMS. Ceramic MEMS use the packaging material as the primary building material.
- **Flexible Manufacturing:** The integration CAD/CAM, CNC and laser machining, and screen printing offers considerable flexibility in design and manufacturing.
- **Rapid Prototyping**: One can go from a design to a prototype in the matter of hours.
- **Inexpensive:** Clean rooms are not needed.
- **Compatibility with Silane Chemistry**: Amendable to immobilization of biological materials.

A Micro/Meso Technology with Ceramic Tapes

- Mechanical Machining (CNC milling & punching)
- Chemical Eetching
- Laser Machining
- Binder Extraction
- Photoforming

- Metallic paths, conductors, thermistors, electrodes, passive electronics, resistors screen-printed & co-fired or vapor deposited on post-fired tapes

Inexpensive, flexible, meso-scale integrated systems

Hybrid Technology:
- **Layered Manufacturing**
- **Rapid Prototyping**
- Bonding to glass, silicon, & alumina
- Embedding of others materials

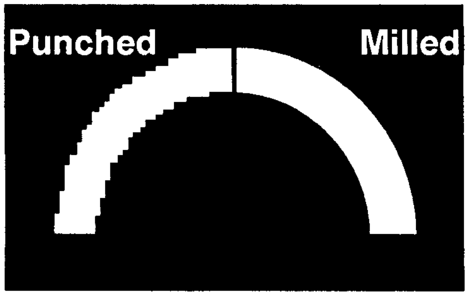
- Meso-scale assembly to attach components that cannot be built within the ceramic process

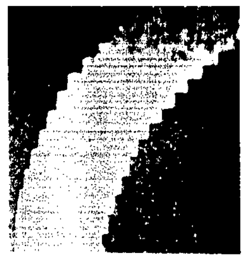
Green Machining

- Mechanical Machining (Milling & Punching)
- Laser Machining
- Chemical Machining by Binder Extraction
- Etching of Partially Fired Tapes
- Photolithography of Photoformable Tapes

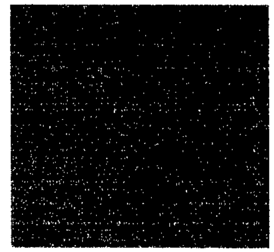
Mechanical Machining of Pre-Fired [illegible]

Machined Samples

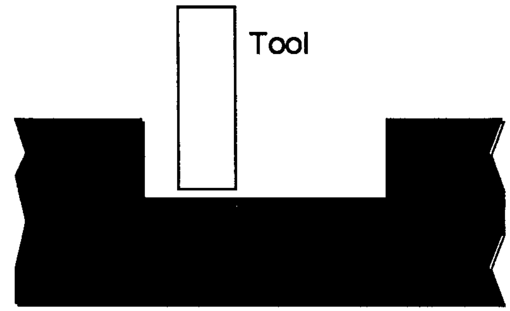




Punched curve



CNC milled curve (two layered structure; the curved slot is in the top layer only)



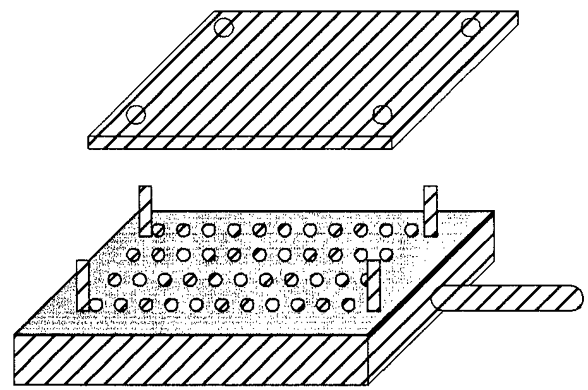
Partial depth CNC milling

PUNCHING

- Circular or square shape
- Smallest size 0.004"(~100microns)
- Machining of curved features is difficult
- Partial depth machining cannot be done

CNC MILLING

- Smallest size 0.005"(~125microns)
- Machining of curved features is easy
- Partial depth penetration facilitating shallow channels and thin membranes
- Vacuum chuck holder is used to fix tape



Vacuum chuck holder for CNC milling

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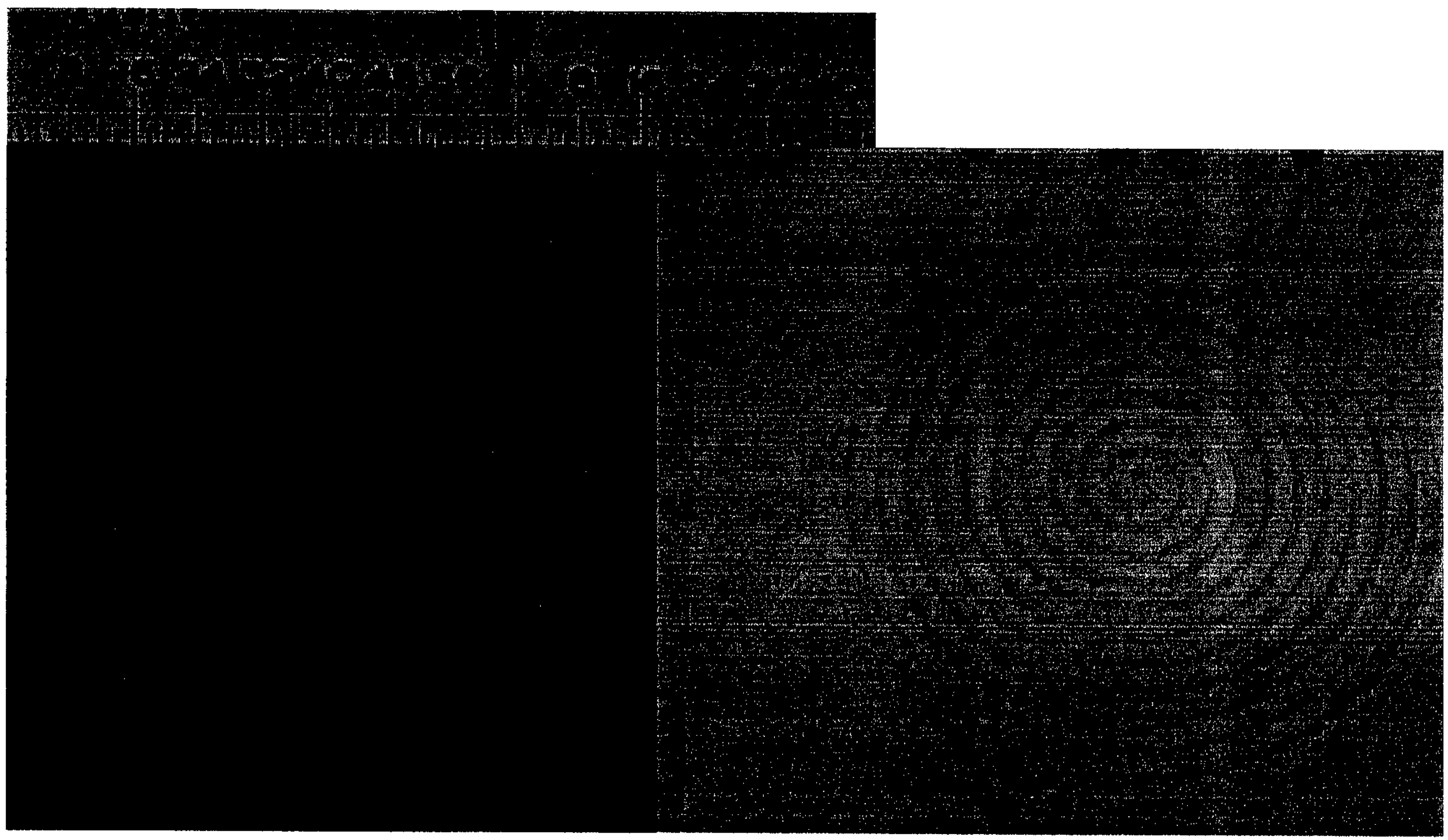
A 200μm*200μm Spiral Milled (left) and Photo-formed (right) in Ceramic Tapes



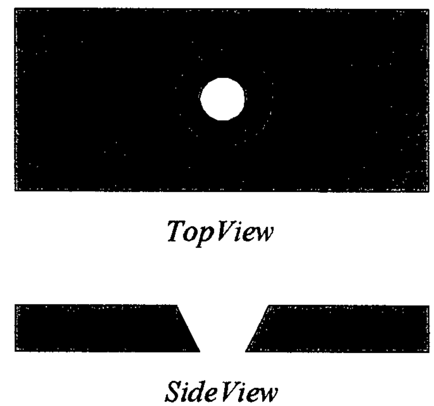
Laser Machining

Nd-Yag Laser

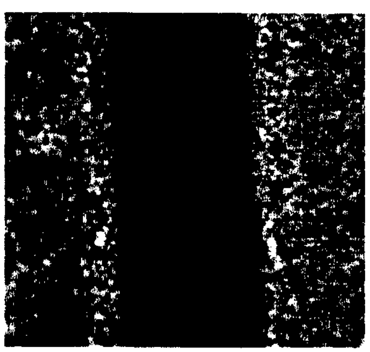
- Thermal machining process

Excimer Laser

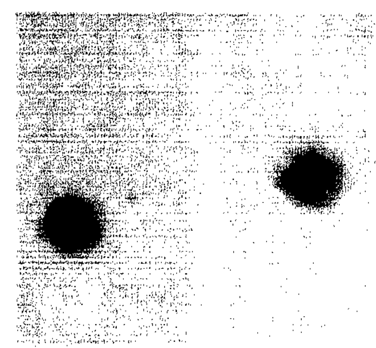
- Smallest size: ~10 microns
- No thermal damage (adiabatic process)
- Machining of whole feature at once using mask
- Partial depth penetration facilitating shallow channels and thin membranes



Schematic of the Laser machined hole



Nd-Yag laser machined sample
(~150 micron wide channel, 20X)



Excimer laser machined sample
(~ 40 micron holes, 20X)

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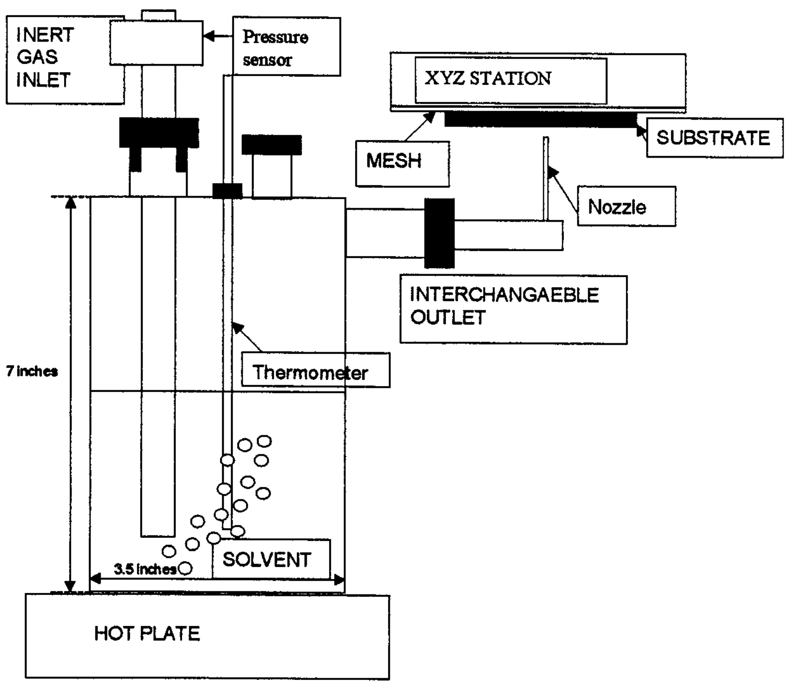
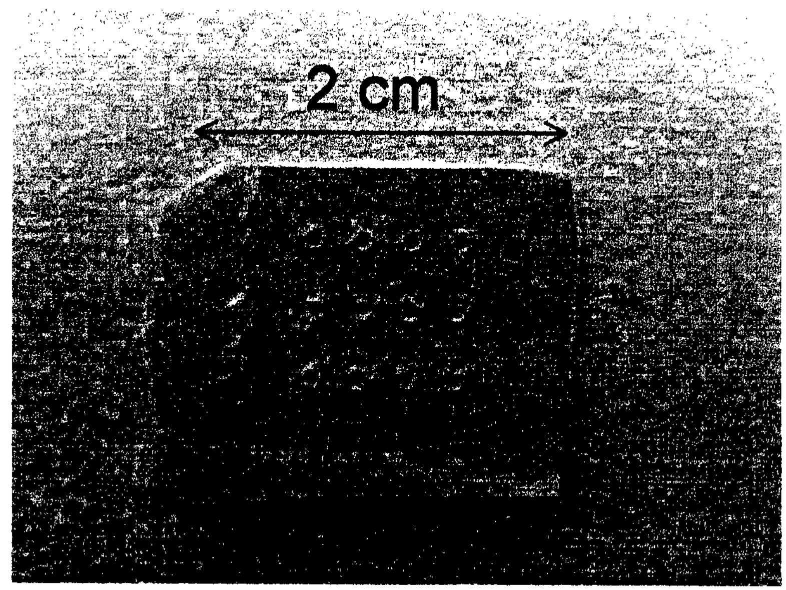
Chemical Machining by Binder Extraction

- **Nitrogen bubbles into the solvent (acetone) that removes the organic binder from the Green Tape.**



Bubbler used for binder extraction.

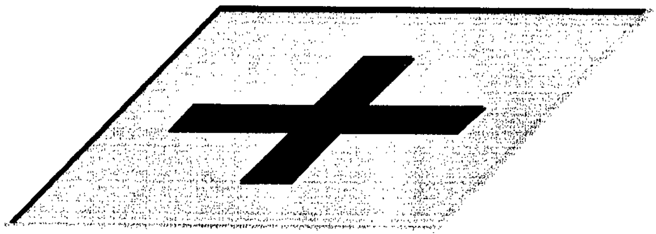


Patterned sample

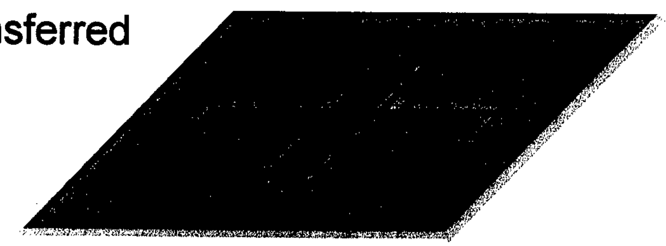
Photoformable Ceramic Tapes

- A negative photoresist material is added to the DuPont 951 tapes as part of the organic binder to create photoformable ceramic tapes
- This new composition makes possible the transfer of patterns from a mask to the green tape using an optical process similar to the photolithography.

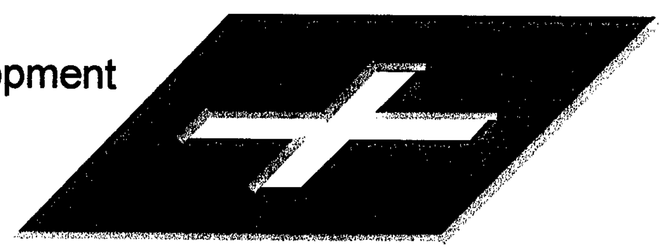
1. Glass mask

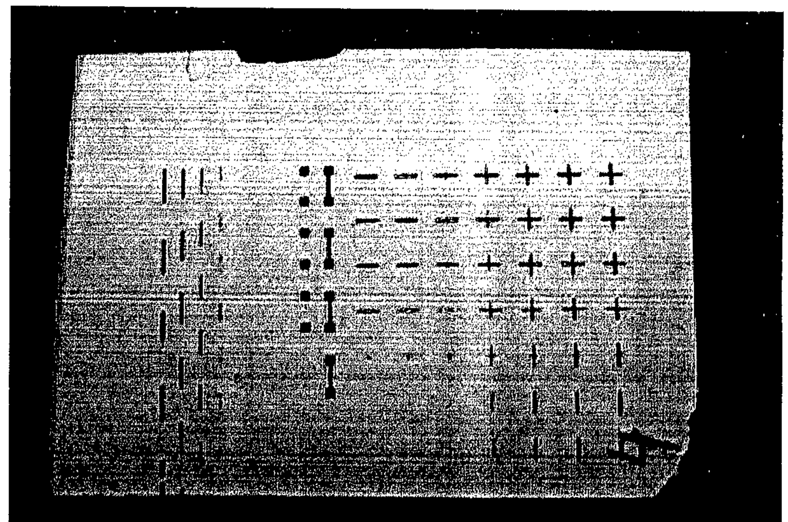


2. Pattern transferred to the tape



3. After development



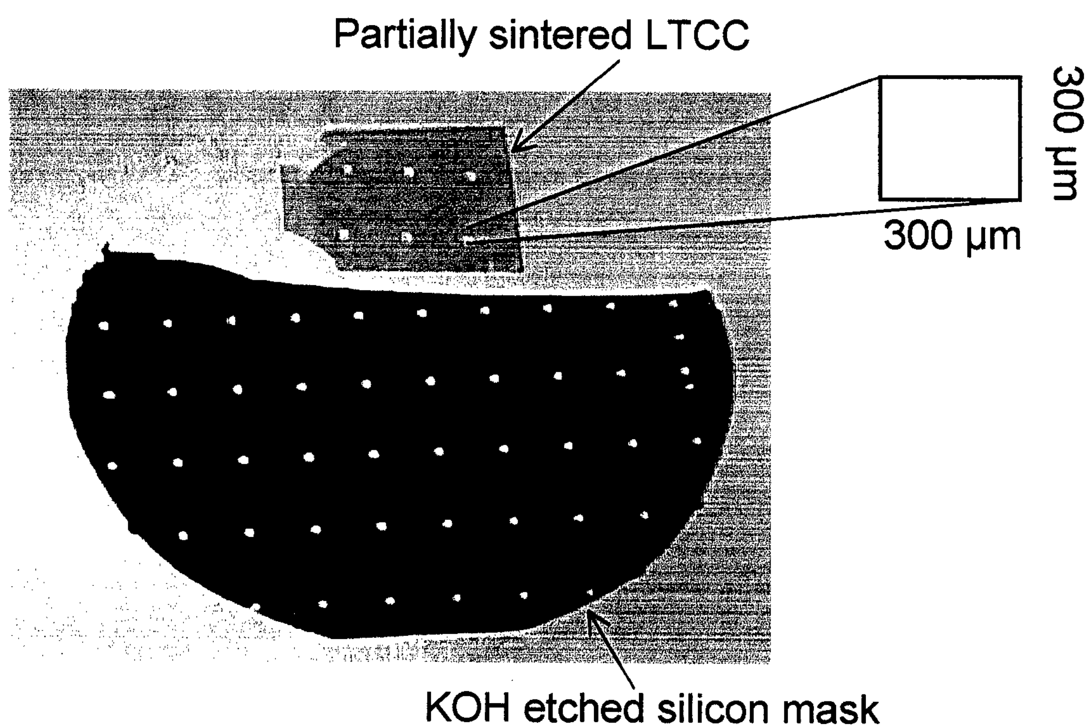


Minimum feature size in this is 70 μm

Pattermed sample using Photoforming technique

Lithography of Partially Sintered LTCC Tapes

The pattern from the anisotropically etched silicon wafer is transferred to the partially sintered LTCC by masking with PMMA, plasma ashing, and etching in BHF



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A FEW PROBLEMS & SOLUTIONS

- Lamination-Induced Deformations

  Solution: sacrificial materials such as a graphite-binder mixture.

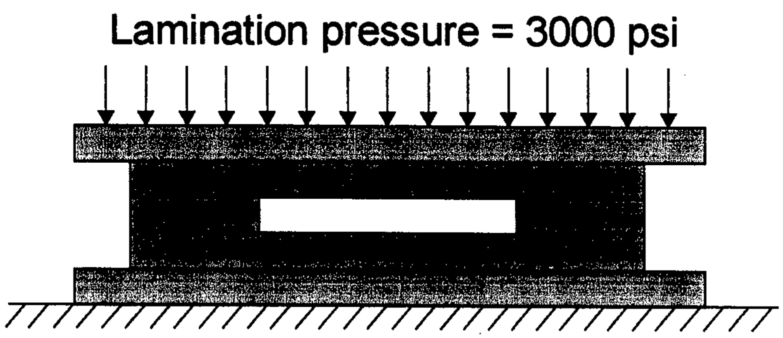
- Fire- induced deformations. Problematic only for large cavities.

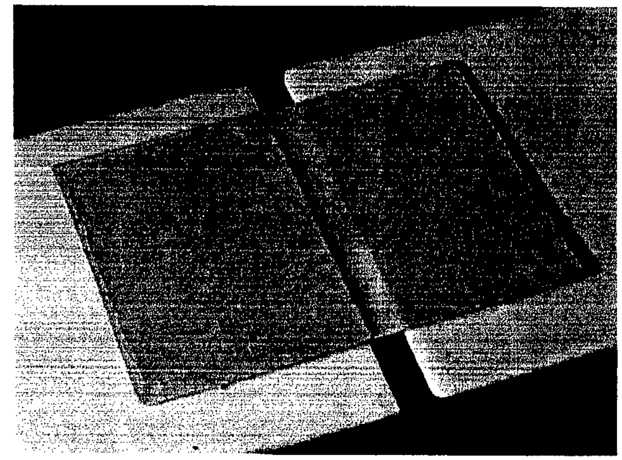
  Solution: Use of sacrificial materials and atmosphere-controlled oven.

- Shrinkage

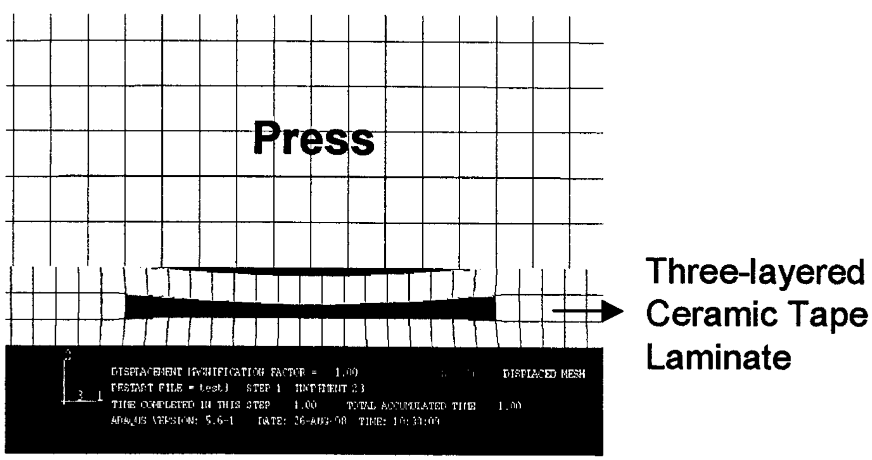
  Solution: compensated by design. Shrinkage can also be controlled by bonding to post-fired ceramics. High precision features can be machined in the post-fired ceramics.

Lamination Induced Deformation

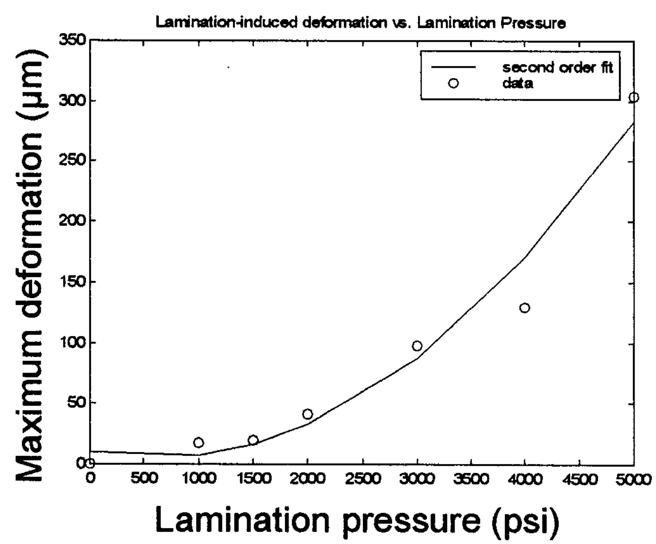




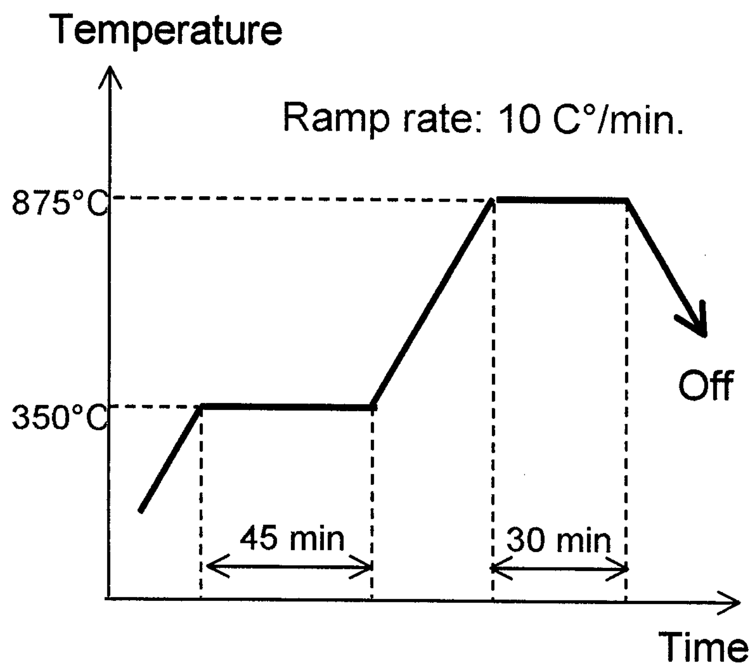
Sample deformed [illegible]



ABAQUS Finite Element Simulation

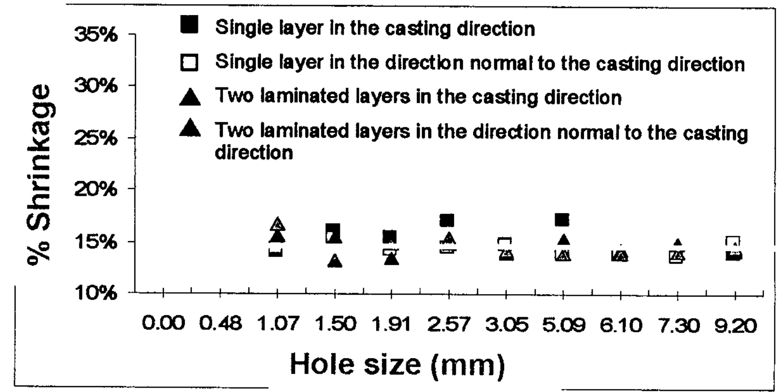


FIRING PROCESS

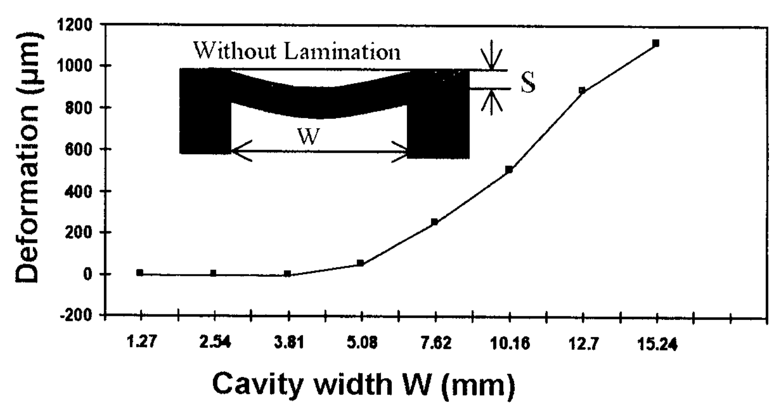


● Programmed Temperature History

● **Shrinkage** of circular holes as a function of hole size



● Firing induced deformation as a function of cavity width



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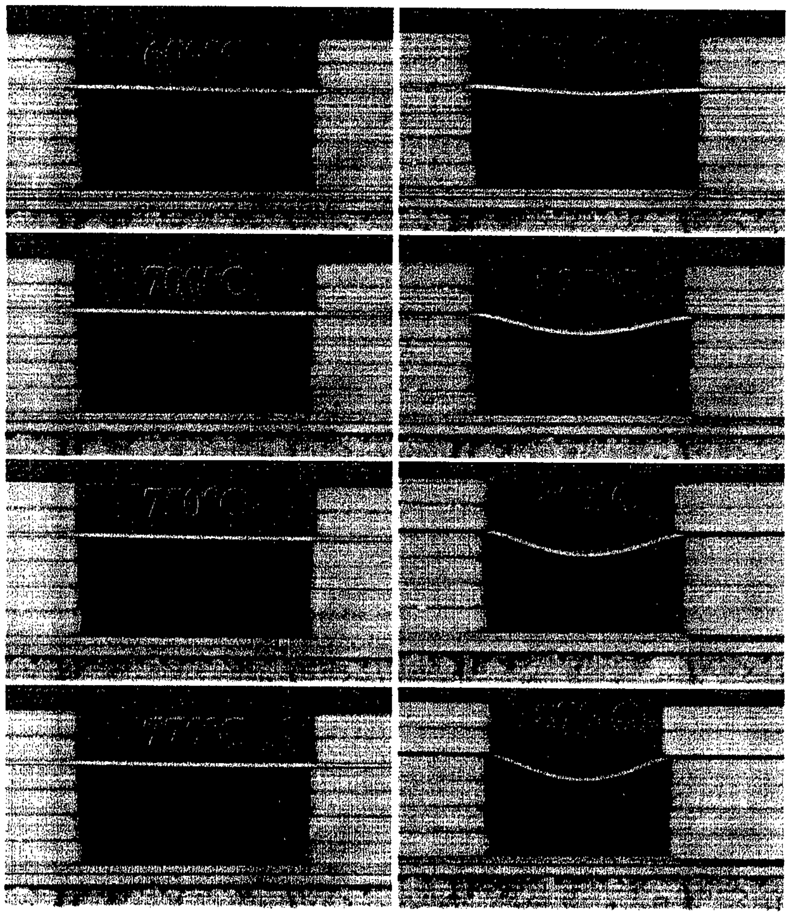
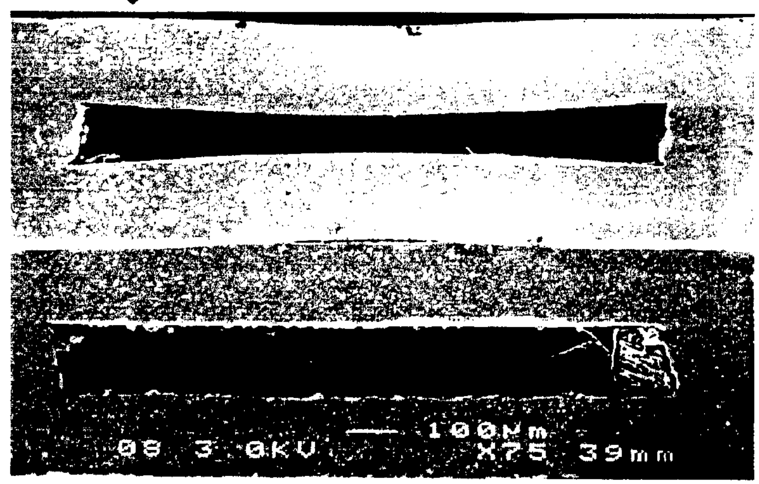
Firing-Induced Deformation and Its Control

- Firing induced deformation as a function of temperature



- Use of graphite-binder mixture to mitigate deformation

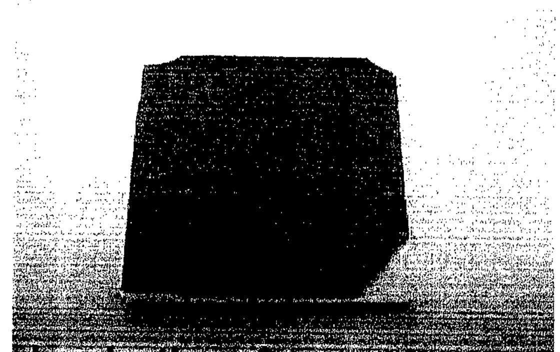
without graphite



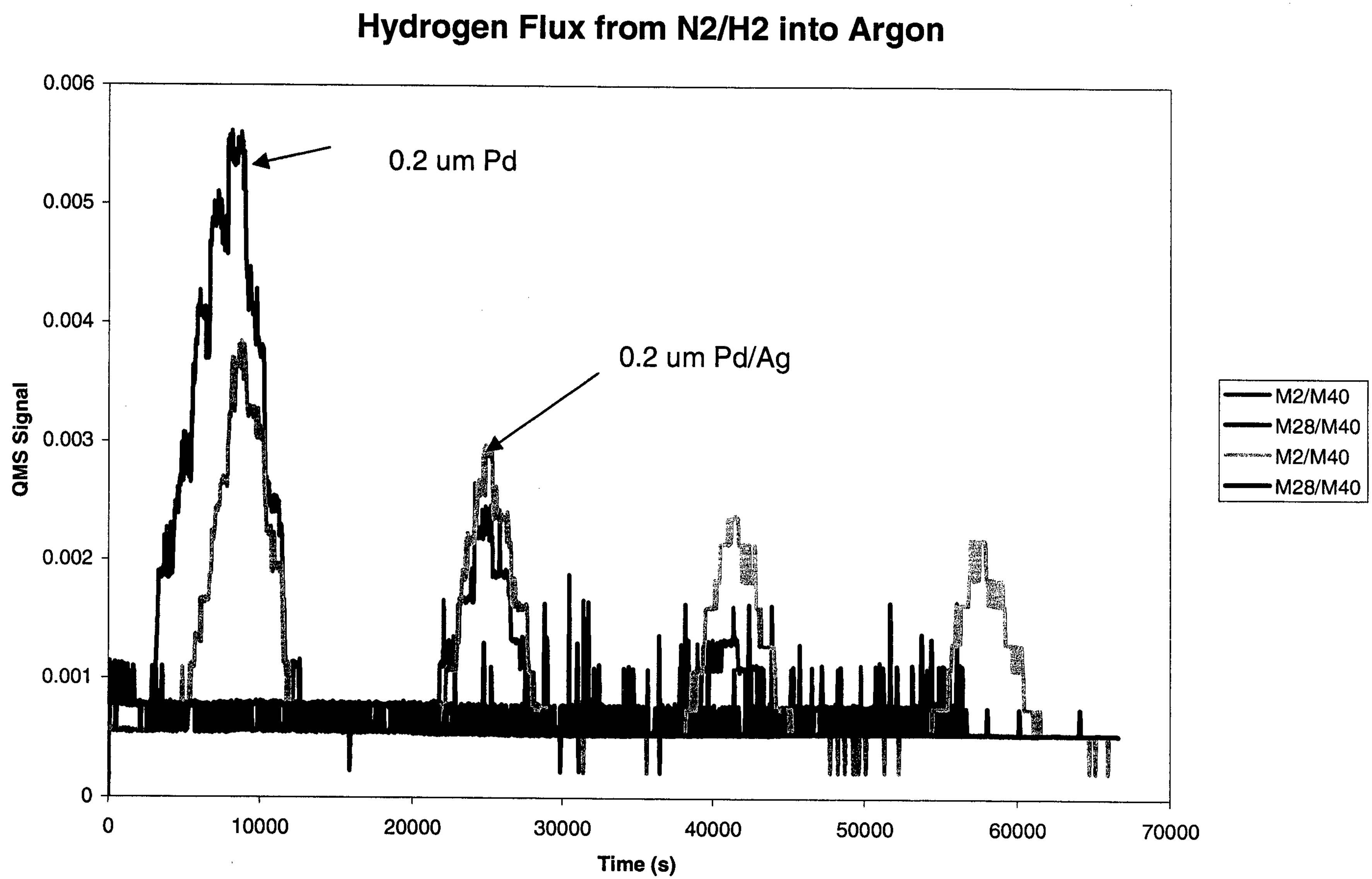
with graphite

A FEW BONDING OPTIONS

- Metallization and Brazing
- Soft Glass
- Epoxy
- High Temperature Bonding with Glass
- Lamination and co-firing with various materials such as alumina, kovar, and post-fired tapes



Lamination of a green tape to an alumina plate followed by firing



Hydrogen Flux from N2/H2 into Argon
0.2 um Pd
0.2 um Pd/Ag
QMS Signal
0.006
0.005
0.004
0.003
0.002
0.001
0
0
10000
20000
30000
40000
50000
60000
70000
Time (s)
M2/M40
M28/M40
M2/M40
M28/M40

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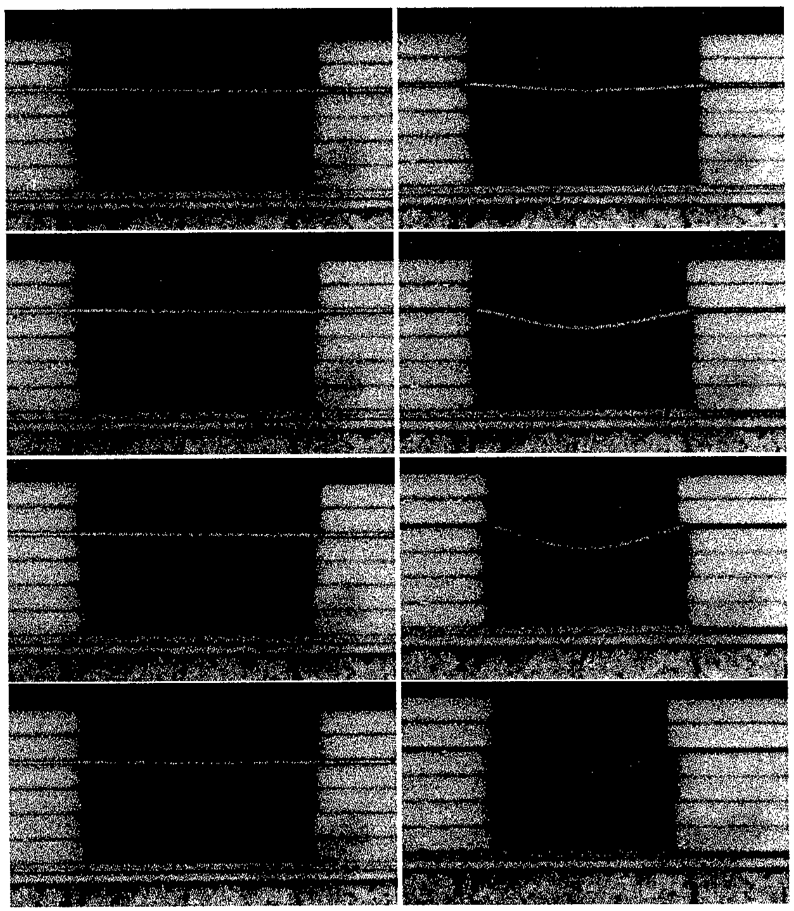
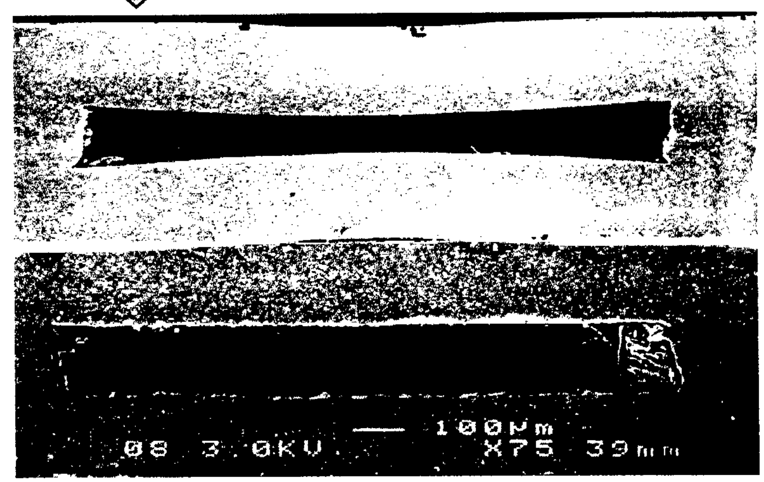
Firing-Induced Deformation and Its Control

- Firing induced deformation as a function of temperature



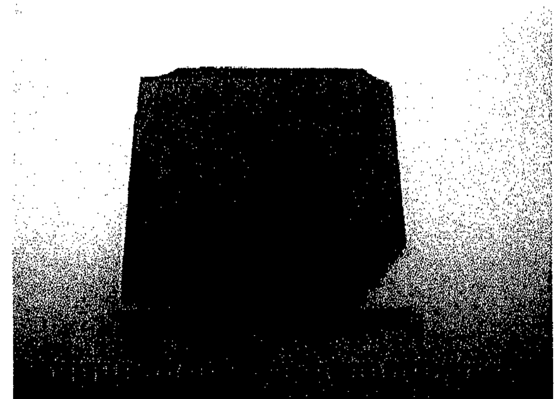
- Use of graphite-binder mixture to mitigate deformation

without graphite



with graphite

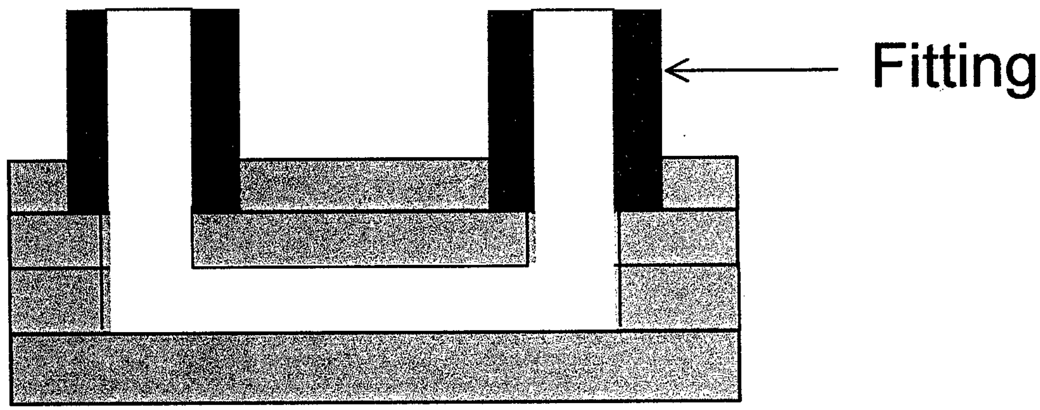
A FEW BONDING OPTIONS



an alumina plate followed by firing

- Metallization and Brazing
- Soft Glass
- Epoxy
- High Temperature Bonding with Glass
- Lamination and co-firing with various materials such as alumina, kovar, and post-fired tapes

Glass and Metal Fittings



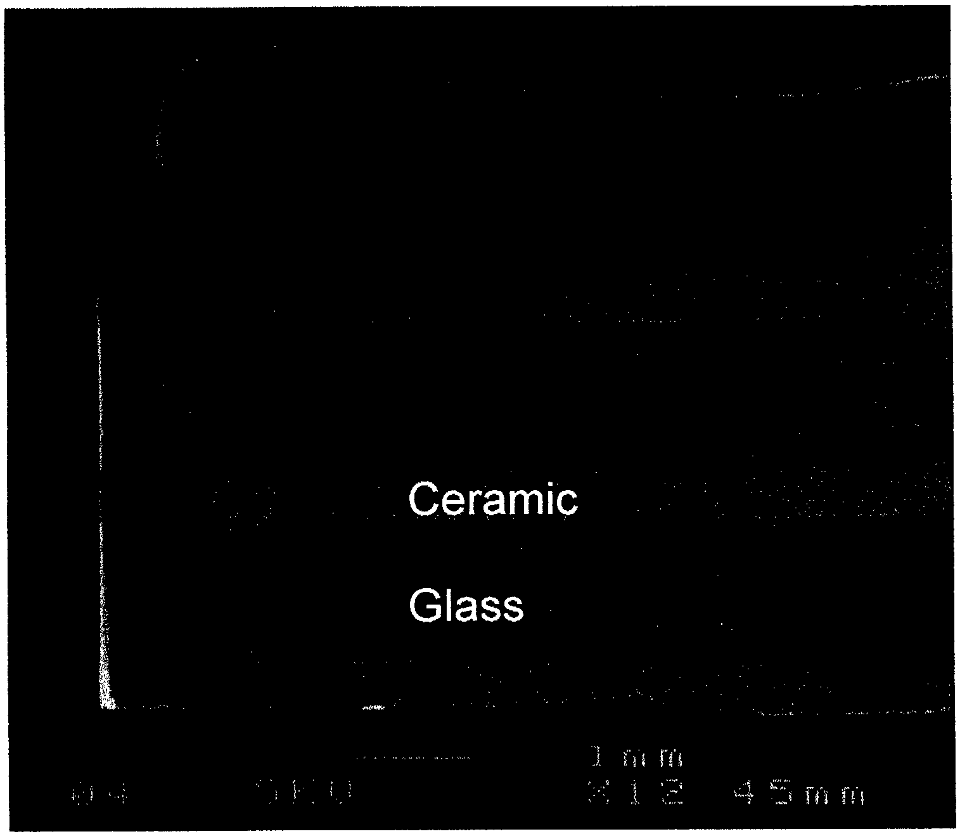
Various Bonding Options

1. Epoxy Bonding

2. Soft Glass

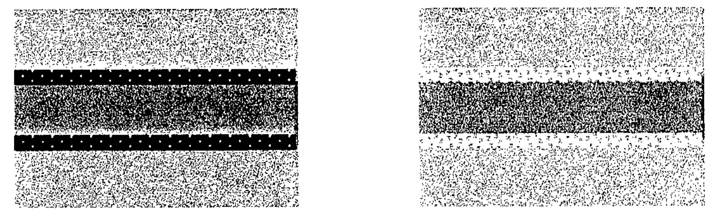
3. Metallization and Brazing

Multi-layered Structures with Glass, Metals and Ceramic Tapes



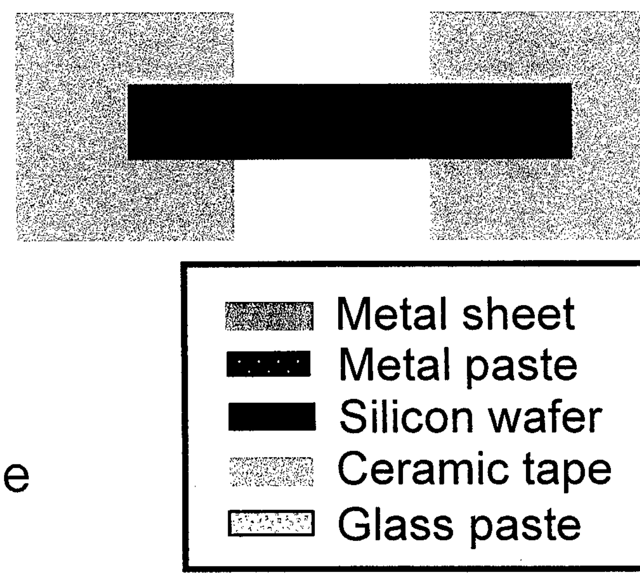
SEM of the multi-layered glass-ceramic sample

Multilayers consisting of Tape & Metals

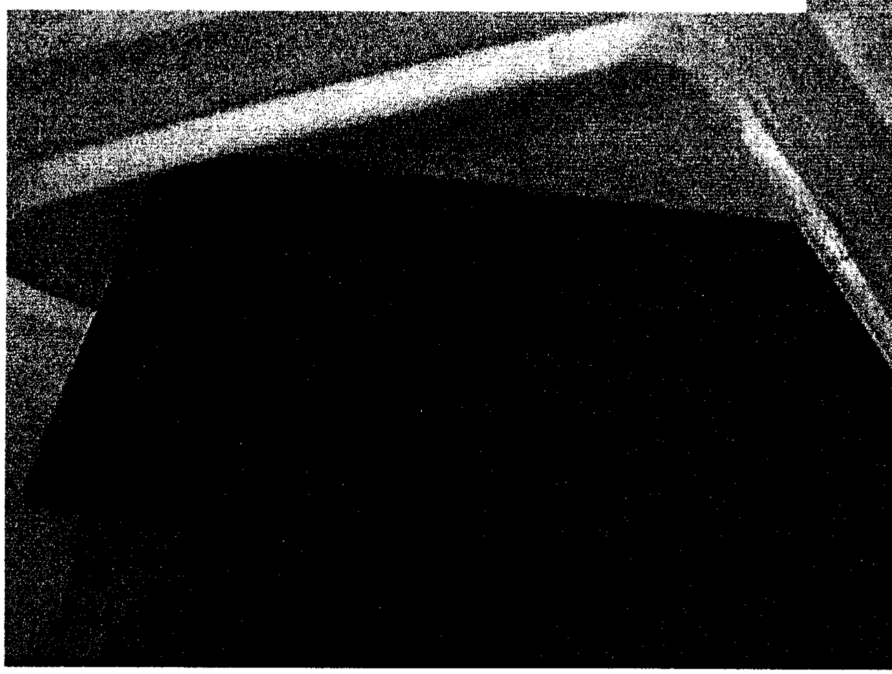


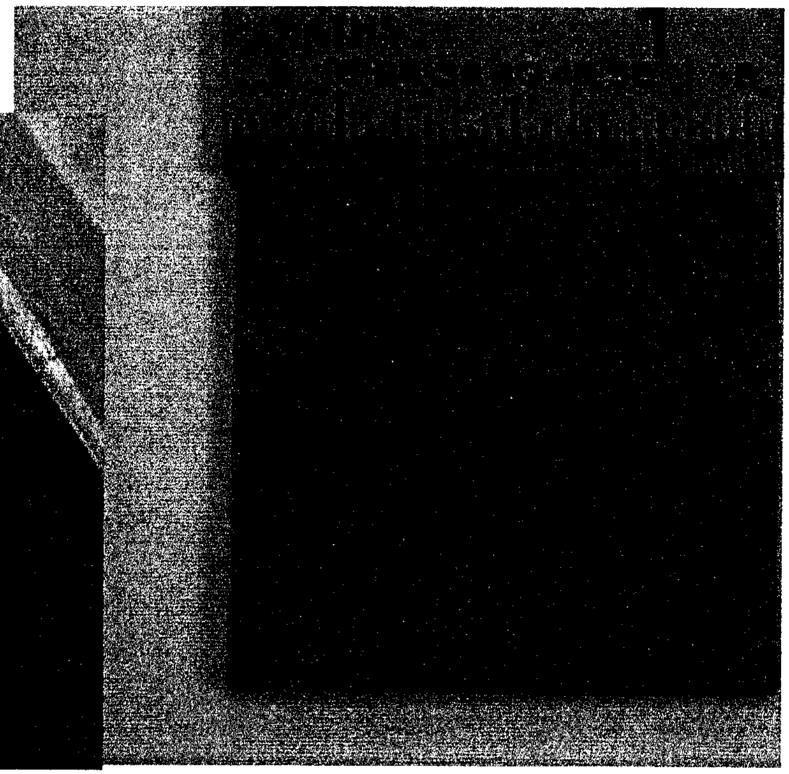
Metal Paste Brazing   Glass Paste Interlayer

Multilayers of Tapes & Silicon Wafer

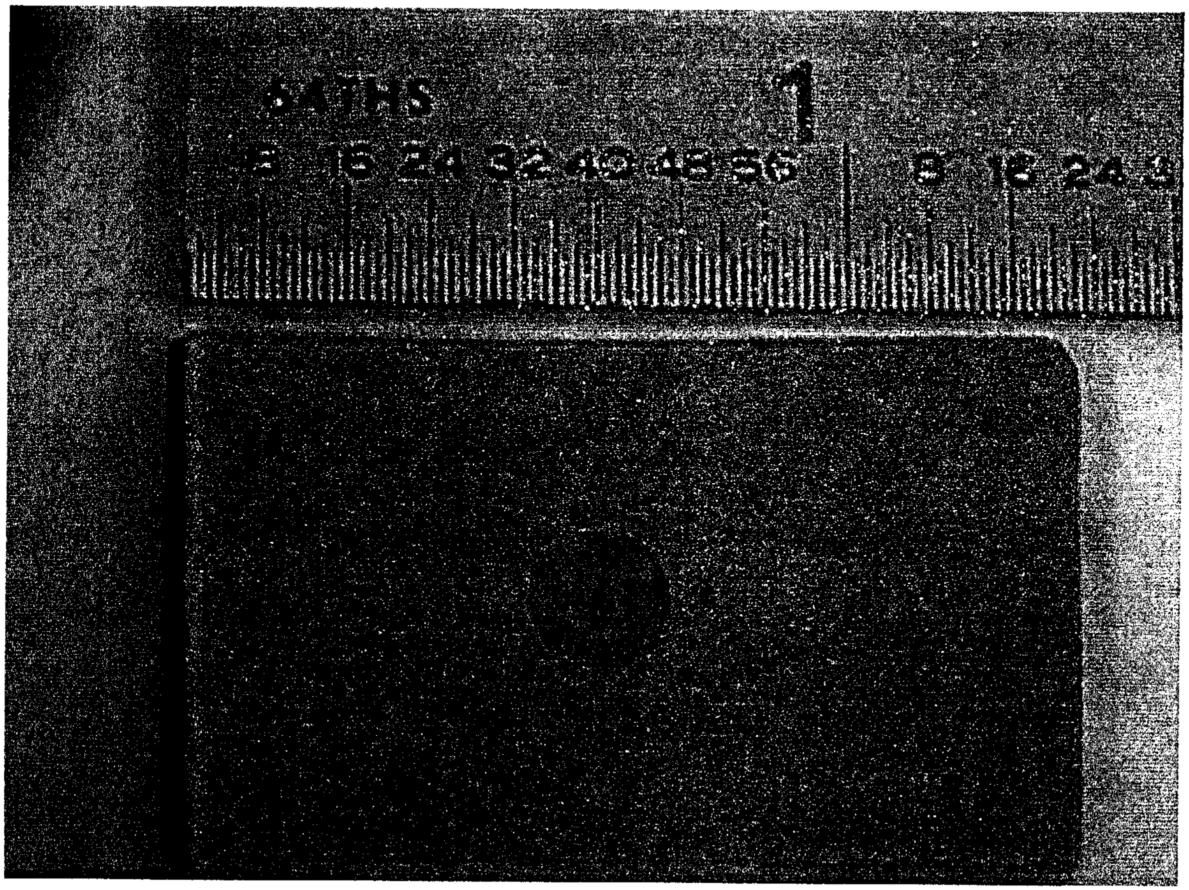


Silicon Plate Sandwiched Between and co-Fired with LTCC





Kovar (Fe54/Ni29/Co17) Plate Sandwiched Between and co-Fired with LTCC

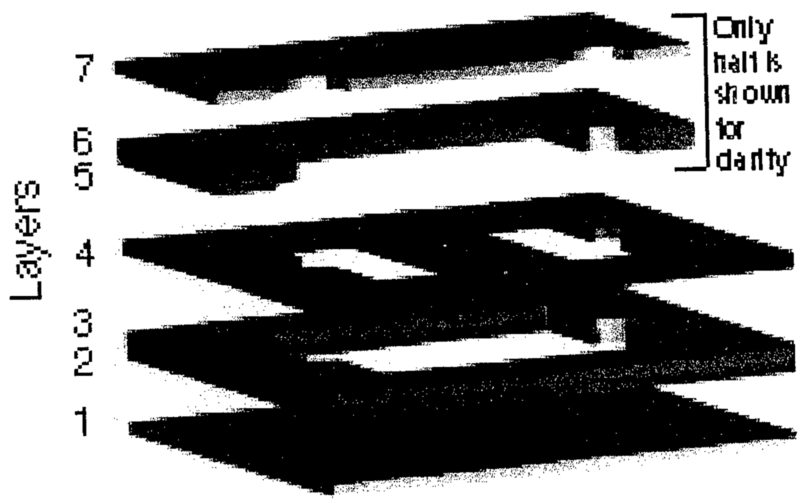


A SAMPLE OF MICROFLUIDIC COMPONENTS FABRICATED IN CERAMIC TAPES

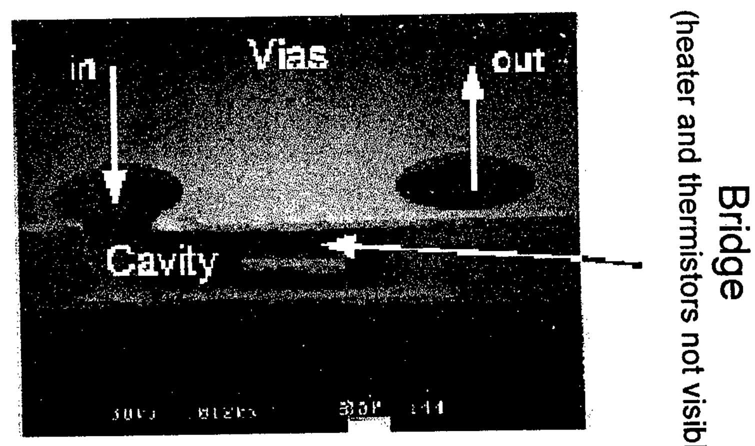
- Hydraulic interconnects
- Thermal flow meter
- Thermal cycler & PCR reactor
- Electrophoretic cell
- Impactor for inertial separation of Particles
- Mixer
- Electromagnetic Actuators

A Thermal Flow Meter

The device consists of seven laminated layers of DuPont 951 ceramic tapes. The layers are patterned using punching to create a thermally isolated bridge in a cavity with inlet and outlets ports. A heater and two thermistors are screen printed on the bridge with vias created for electrical connections.



Exploded View



SEM of the manufactured device

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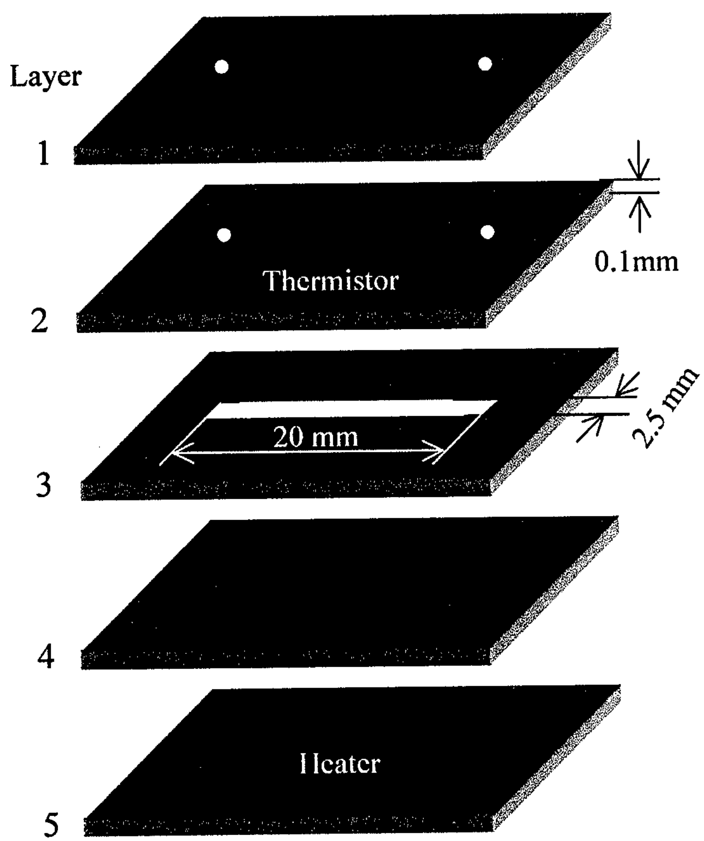
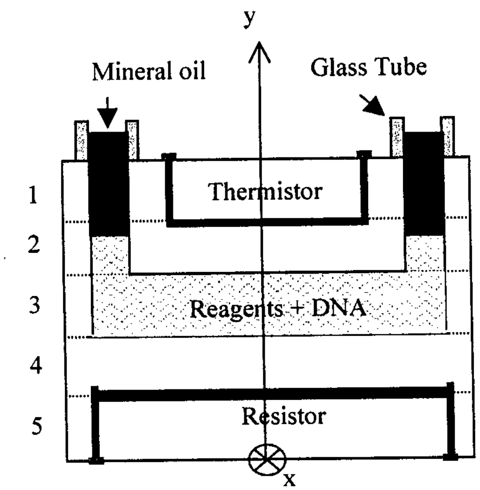
A Thermal Cycler Fabricated in Ceramic Tapes



Exploded View



1(b)

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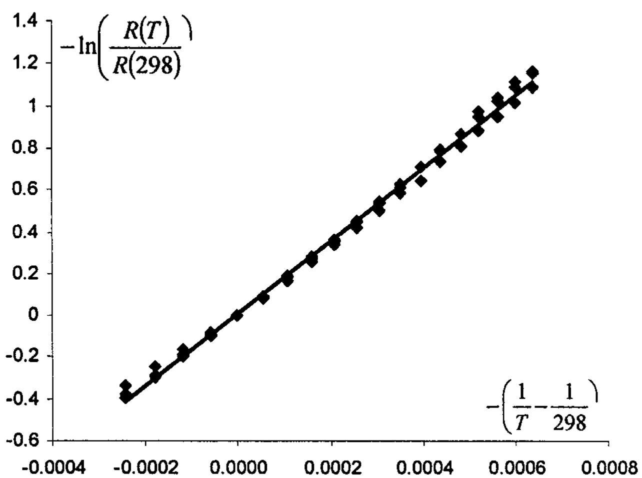
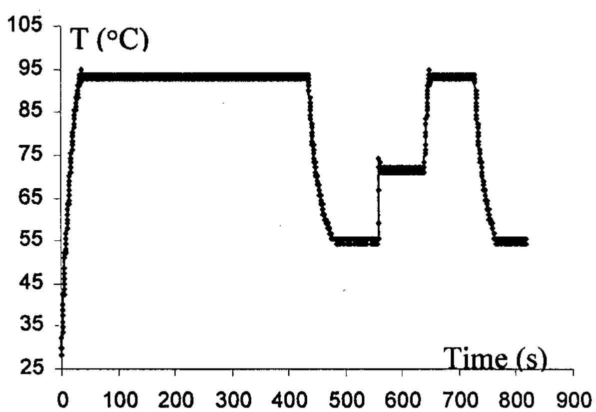
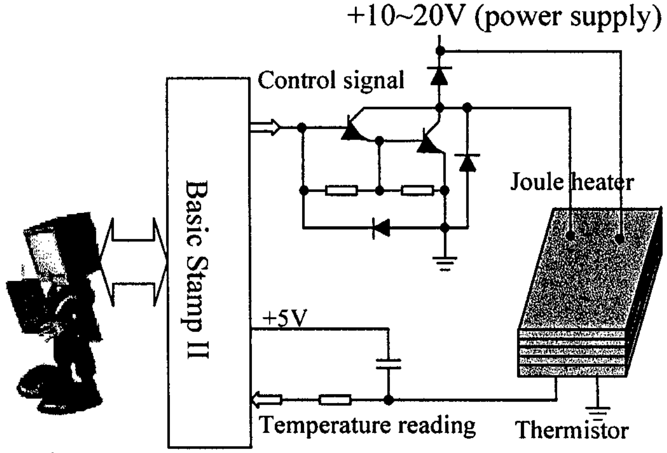
PCR in a Ceramic Chip



Thermistor's Calibration Curve



Temperature Cycling (Measured Data)



Temperature Controller

Gel Electrophoresis

DNA template: Human IL-8
A: Ceramic Chip; B: commercial PCR;
C: Marker

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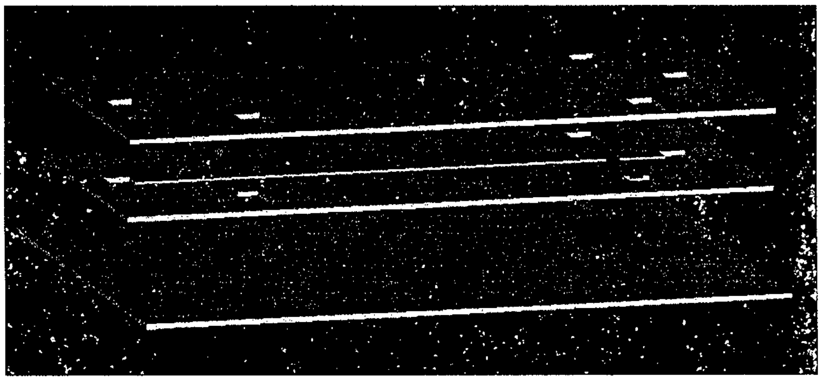
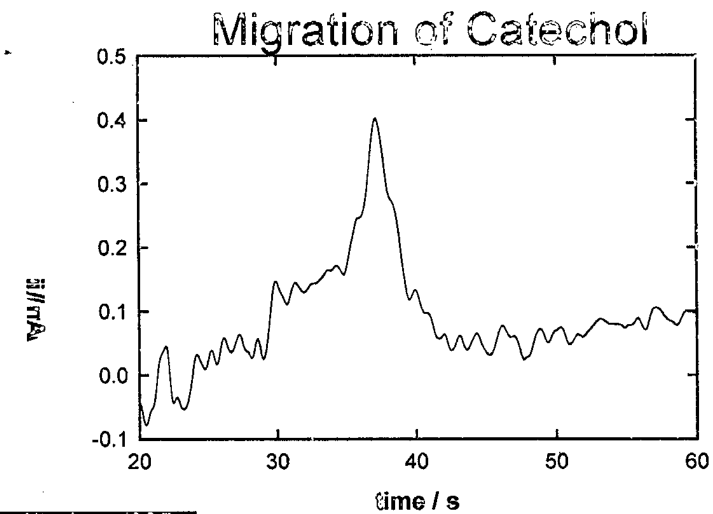
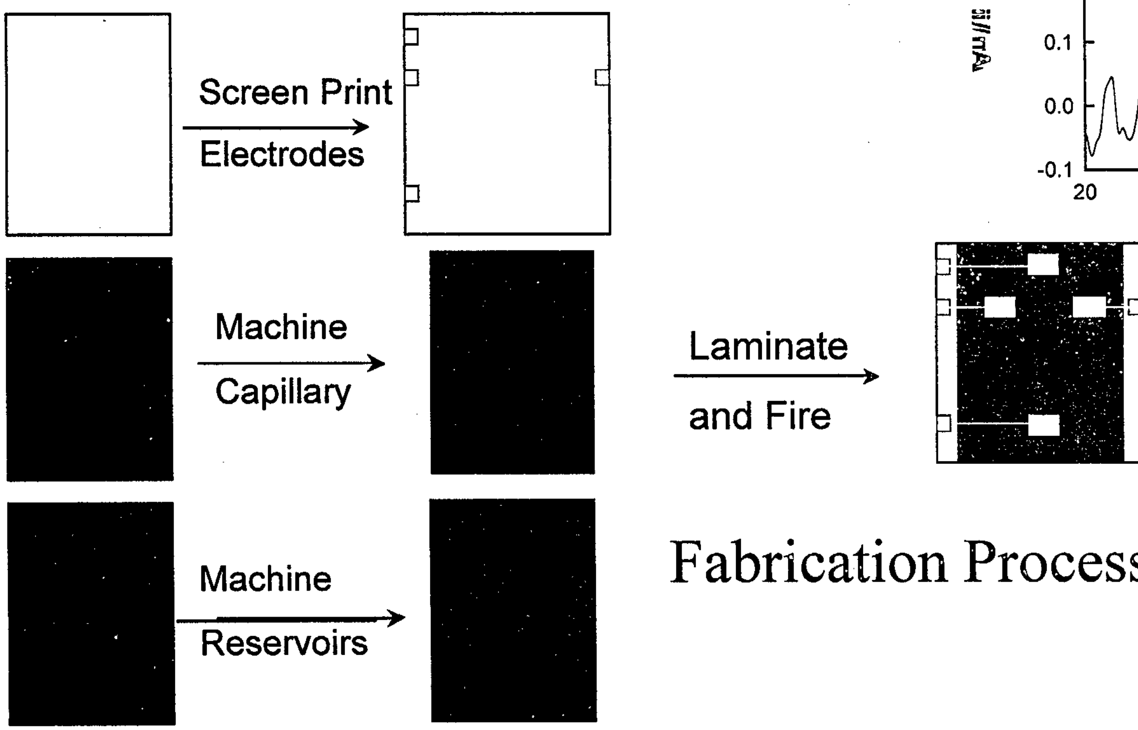
Capillary Electrophoresis in a Ceramic Channels



In collaboration with Charles S. Henry, Min Zhong, and Susan M. Lunte,
Department of Pharmaceutical Chemistry, University of Kansas, Lawrence, KS.





Fabrication Process

Capillary pretreatment:
- 30 min, 0.1 M NaOH

Separation Conditions:
- 500 V (167 V/cm)
- 20 mM TES buffer, pH 7.0
- 25 μM catechol (neutral marker)
- +0.8 V detection potential (Vs. Ag wire)

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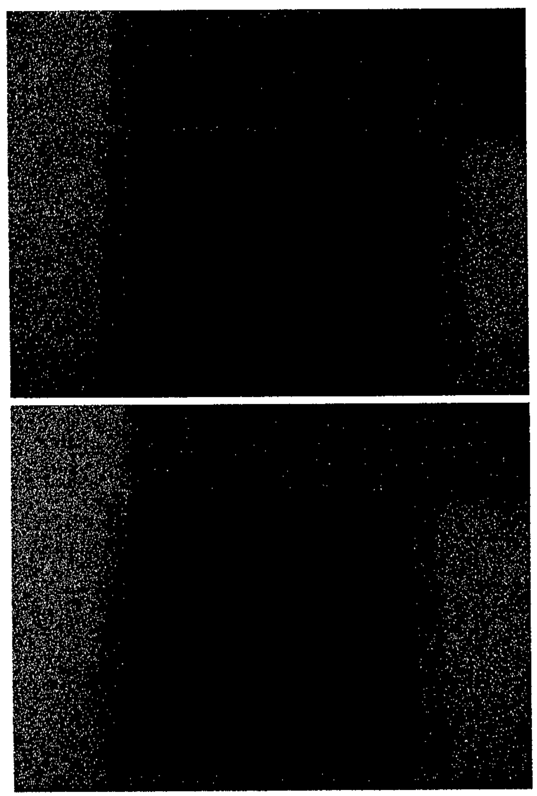
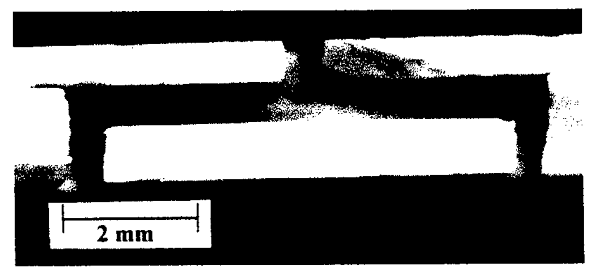
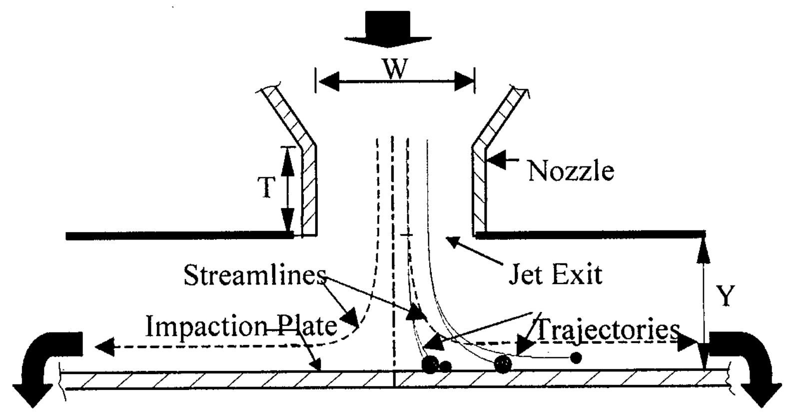
IMPACTOR (Inertial separation of particles from a gas stream)



Top and Bottom Views

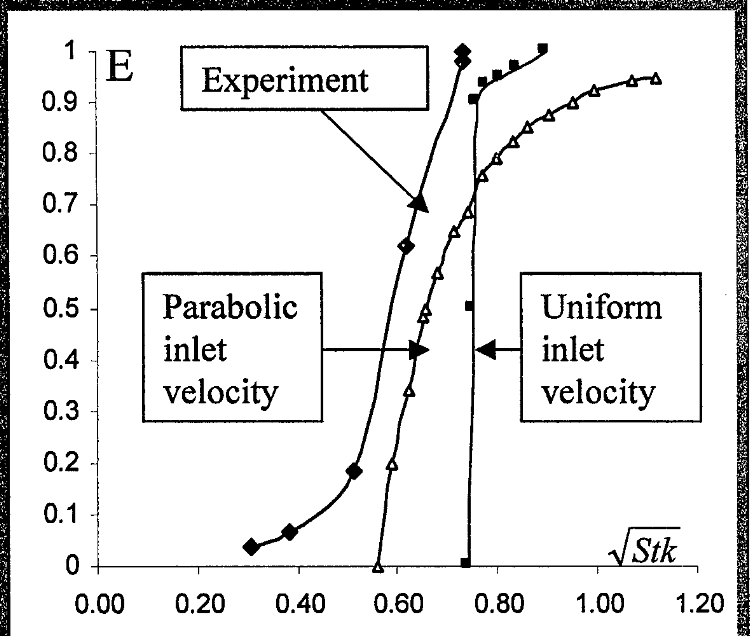


Cross-section of the Impactor

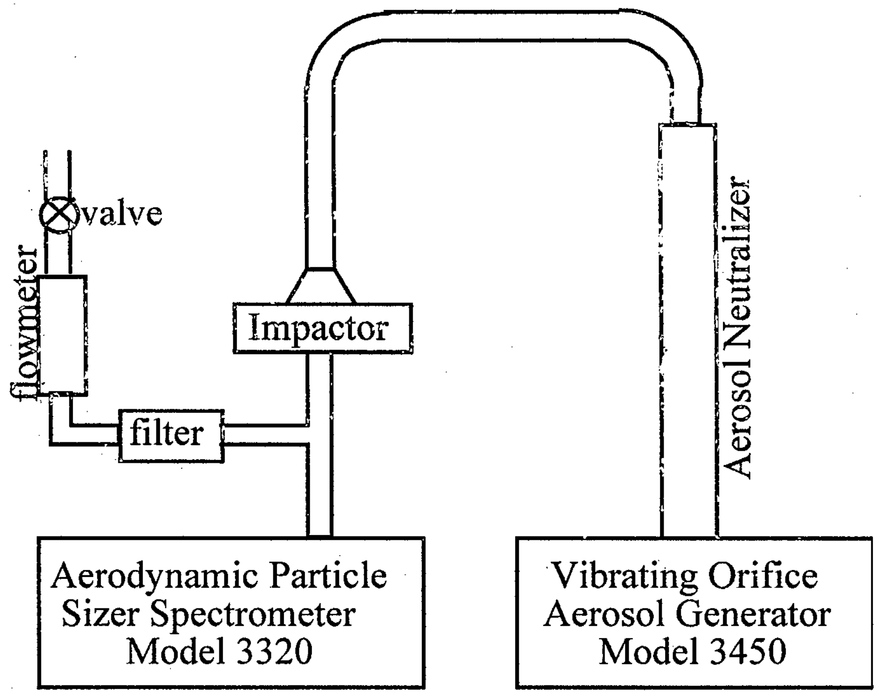


Principle of Operation

Impactor-Testing



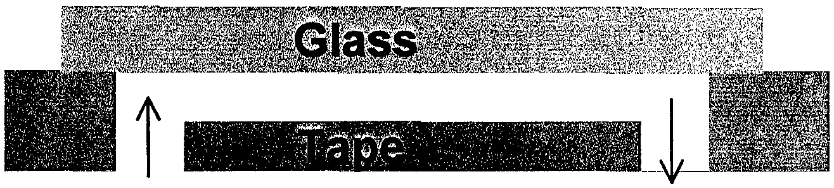
The fraction of collected particles as a function of the Stokes number.

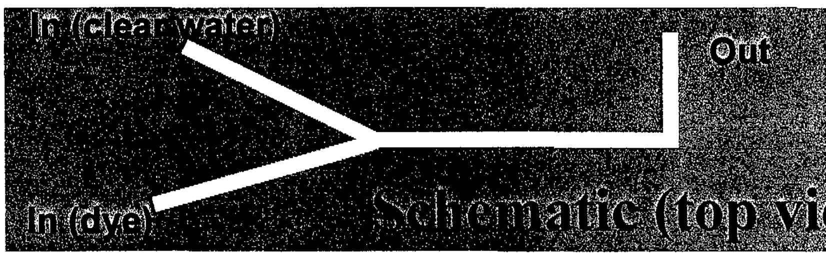


Experimental Set - Up

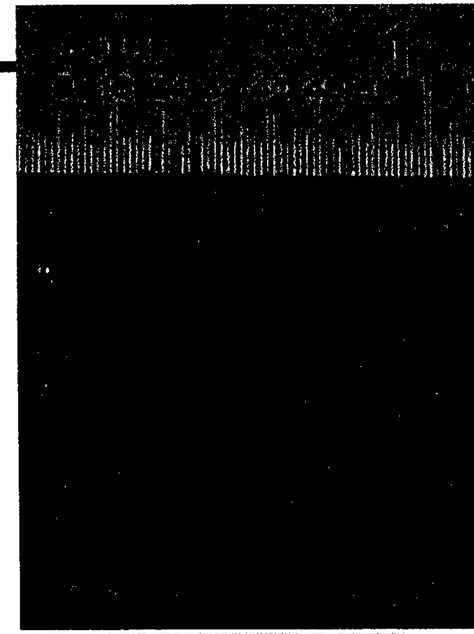
Visualization of the flow in Micro-channels Fabricated in Ceramic Tapes

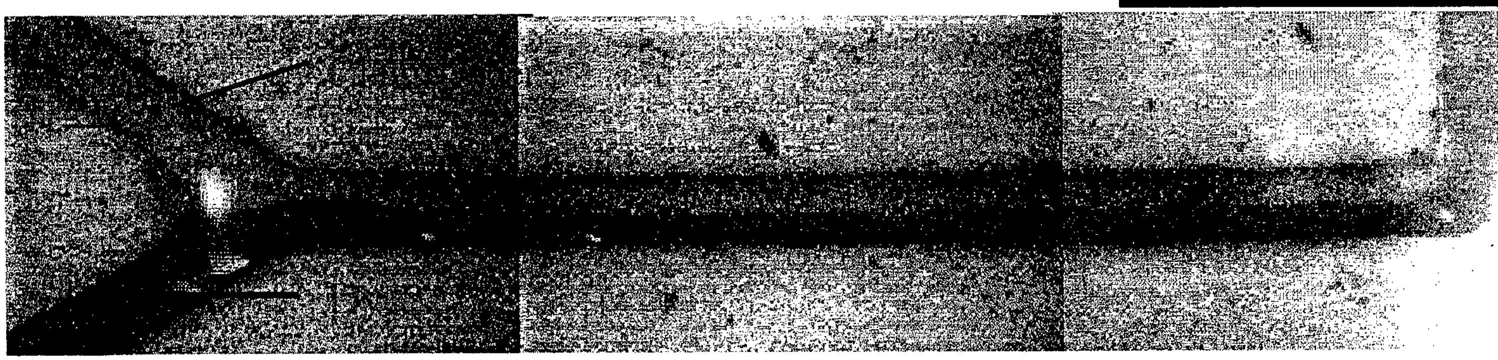
Schematic (side view)





Schematic (top view)

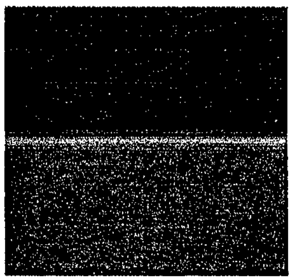




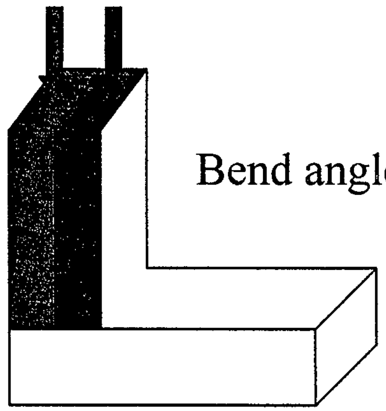
Channel cross-section: 200μm×200μm

Re≈30

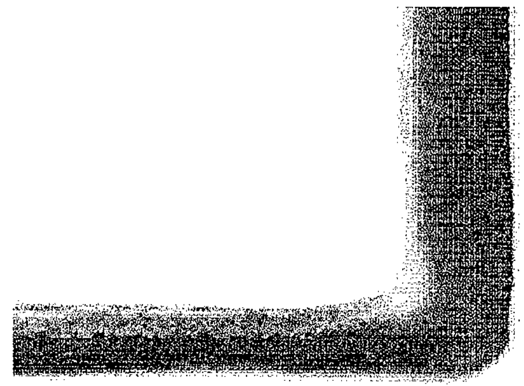
Mixing of Two Fluids Passing a Micro Bend Modeling and Visualization



Distribution of A & B at inlet



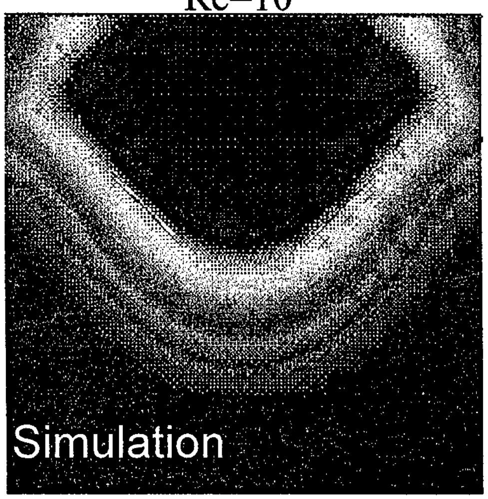
Bend angle=90°



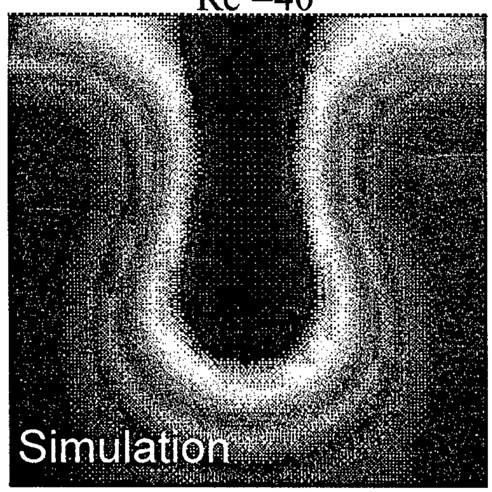
Experiment

Distribution of A & B at outlet

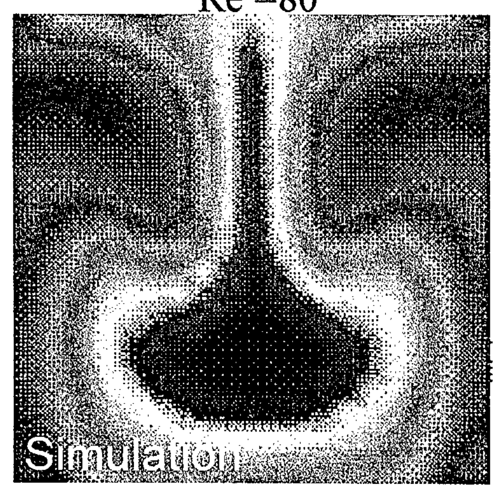
Re=10



Re =40

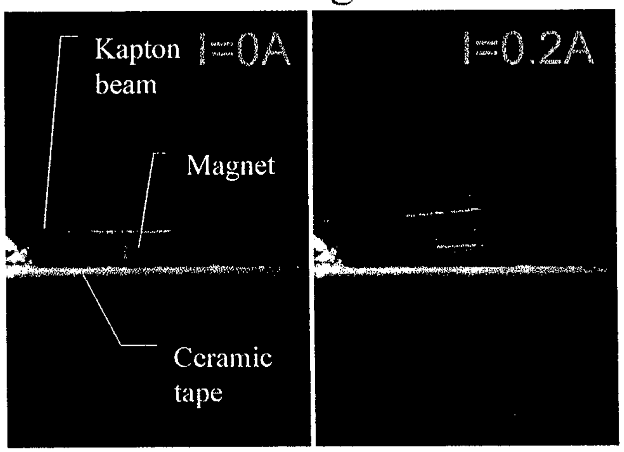


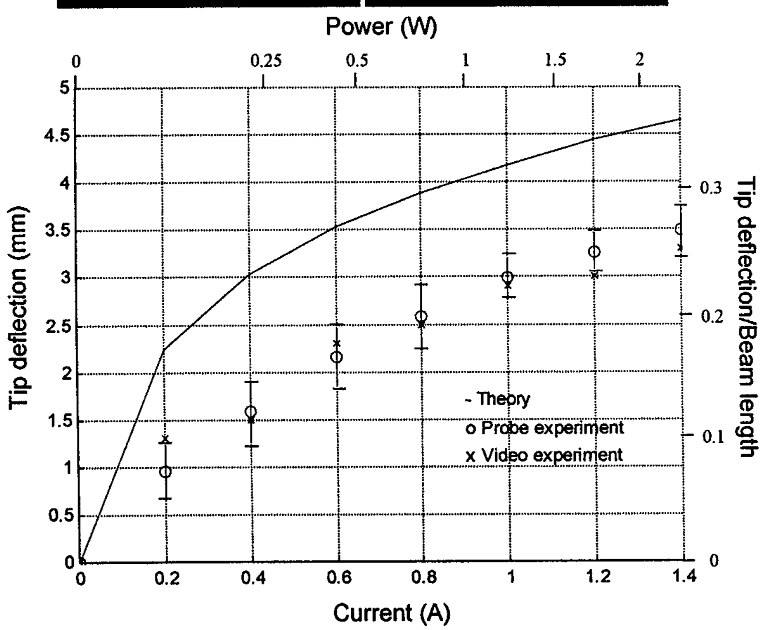
Re =80



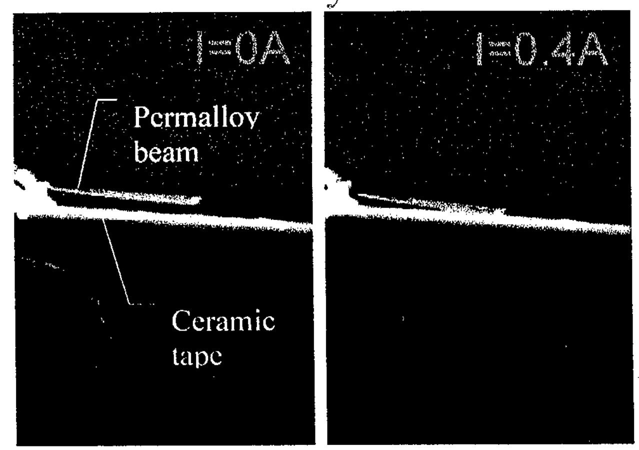
Electromagnetic Actuators

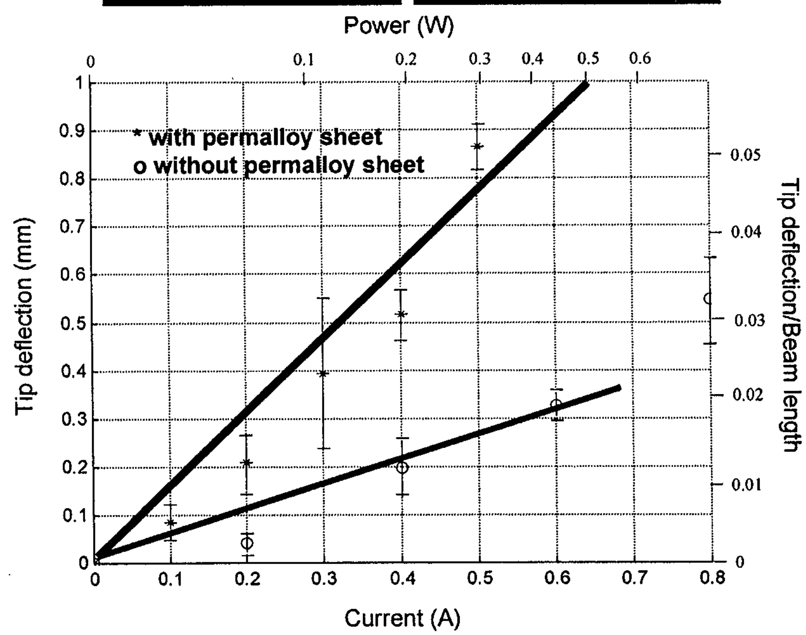
Permanent magnet actuator





Permalloy actuator





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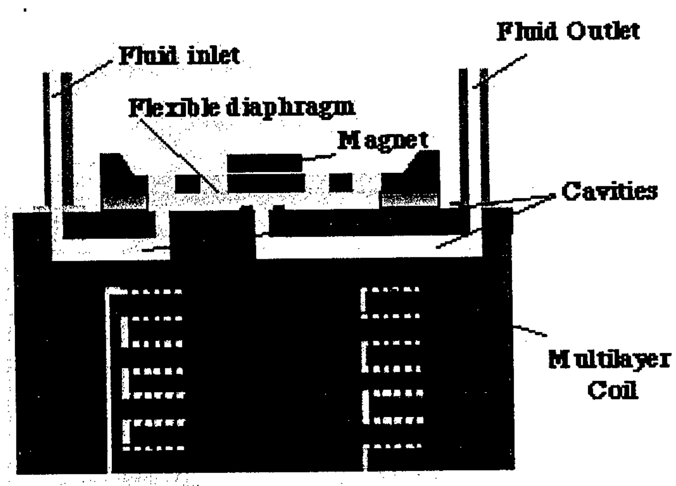
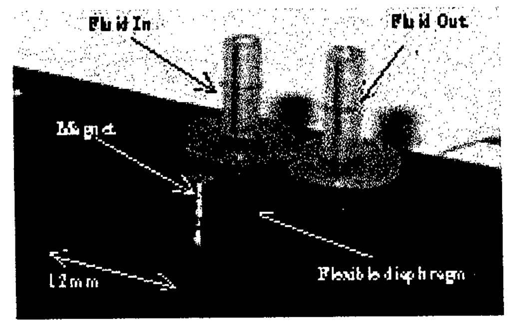
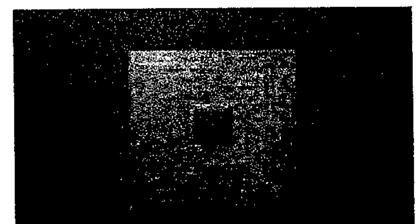
Electromagnetically Actuated Valve

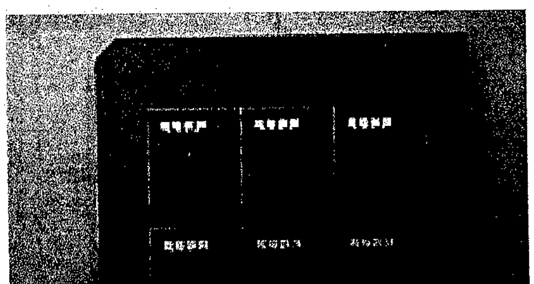


This actuator is a three dimensional hybrid system achieved with LTCC tapes, screen printing and silicon anisotropic etching.

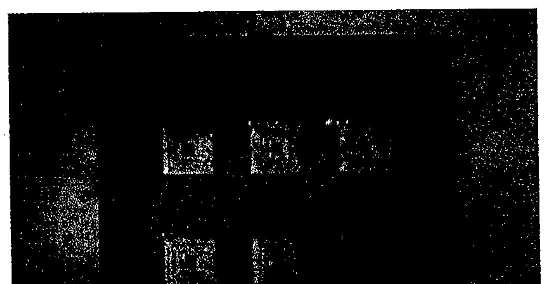




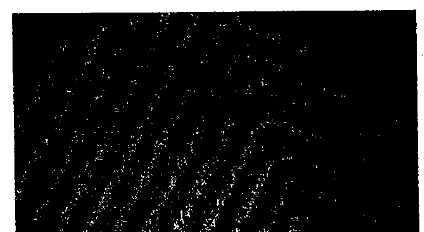
One square planar coil with 20 turns.



An LTCC EM assembly consisting of 6 coil each formed by laminating 7 layers.



A planar coil layer of silver conductors of 80 µm width and pitch and 10 µm thickness



Detail of conductors, note via connection at the tail end.

550

Publications

- Gongora-Rubio, M., Sola-Laguna, L.M., Moffett, P.J., Santiago-Aviles, J.J. "The utilization of low temperature co-fired ceramics (LTCC-ML) technology for meso scale EMS, a simple thermistor based flow sensor." *Sensors & Actuators*, 73, p215, 1999.

- Espinoza-Vallejos, P., Zhong, J., Gongora-Rubio, M., Sola-Laguna, L.M., Moffett, P.J., Santiago-Aviles, J.J. "Meso (Intermediate)-Scale Electromechanical Systems for the Measurement and Control of Sagging in LTCC Structures." *MRS Conf. Proceedings*, Vol. 518, p517, (1998).

- Lynch, H., Park, J., Espinoza-Valejos, P.A., Santiago-Aviles, J.J., Sola-Laguna, L. "Meso-Scale Pressure Transducers Utilizing Low Temperature Co-Fired Ceramic Tapes." *MRS Conf. Proc., Symposium AA* (1998).

- Park, J., Espinoza-Valejos.P.A., Sola-Laguna, L., Moffett, P.J., Santiago-Aviles, J. "Etching and Exfoliation Techniques for the Fabrication of 3-D Meso-Scales Structures on LTCC Tapes." *Proc. IMAPS 98*, San Diego, Vol 98, pp 42.

- Gongora-Rubio, M., Sola-Laguna, L.M., Santiago-Aviles, J.J. "A Meso-Scale Electro-magnetically Actuated Normally Closed Valve Realized on LTCC Tapes." Submitted to *4 Micro Fluidic Devices and Systems (MF04)*.

- Espinoza-Vallejos, P., Sola-Laguna, L.M., Moffett, P.J., Santiago-Aviles, J.J. "Simulation of Diffusive Light Exposure of LTCC Tapes and the Selection of an Optimal Grain Size Distribution." Accepted for presentation and publication in *IEEE-MSM99 S.J. PR.*

- Espinoza-Vallejos, P., Dimas, C., Santiago-Aviles, J. "Photolithographic Processing of LTCC Tapes." Submitted to *IMPAS 99*, Chicago, IL.

- Charoenmechaikul, S., Luzzi, D.E., "Microstructural Evolution of Co-fired Ceramic Tapes for MEMS Applications", in "Materials Science of Microelectromechanical (MEMS) Devices", eds. A.H. Heuer and S.J. Jacobs, MRS Vol. 546, (1999), in press.

- Bau, H. "Optimization of conduits' shape in micro heat exchangers." *Int. J. Heat and Mass Transfer*, 41, pp. 2717-2723 (1998).

- Bau, H., Ananthasuresh, G.K., Santiago-Aviles, J.J., Zhong, J., Kim, M., Yi, M., Espinoza-Vallejos, P. "Ceramic Tape-Based Systems Technology." *Micro-Electro-Mechanical Systems (MEMS),* DSC-Vol. 66, pp. 491-498 (1998).

- Kim, M., Yi, M., Zhong, J., Bau, H., Hu, H., Ananthasuresh, G.K. "The Fabrication of Flow Conduits in Ceramic Tapes and the Measurement of Fluid Flow Through These Conduits." *Micro-Electro-Mechanical Systems (MEMS),* DSC-Vol. 66, pp. 171-177 (1998).

- Zhong, J., Yi, M., & Bau , H., H., "A Thermal Cycler Fabricated with Low Temperature, Co-Fired Ceramic Tapes," accepted for publication in the proceedings of the 1999 International Mechanical Engineering Conference and Exposition.

- Kim, M., Kim, D., Anathasuresh, S., & Bau, H., H., "Meso-scale Electromagnetic Actuators Fabricated in Low-Temperature, Co-fired Ceramic Tapes," accepted for publication in the proceedings of the 1999 International Mechanical Engineering Conference and Exposition.

- Yi, M., Hu, H., Bau, H., H., & Erickson, K., " theoretical and Experimental Study of Mesoscopic Impactors," accepted for publication in the proceedings of the 1999 International Mechanical Engineering Conference and Exposition.

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Mesoscopic Machines:

There is plenty of room in the middle!

Lawrence H. Dubois

Director, Defense Sciences Office
Defense Advanced Research Projects Agency
Arlington, VA 22203

http://www.darpa.mil

Why Mesoscale Machines -

- *Optimum* size for chemistry / combustion / heat transfer / pumping / electrostatic actuation
- Enhanced heat, mass, and momentum transport
- Improved reliability and lower cost through parallel operation of multiple machines
- Wide materials choice / mixtures of materials
- True 3-dimensional shapes; complex shapes
- Rapid prototyping/absence of tooling

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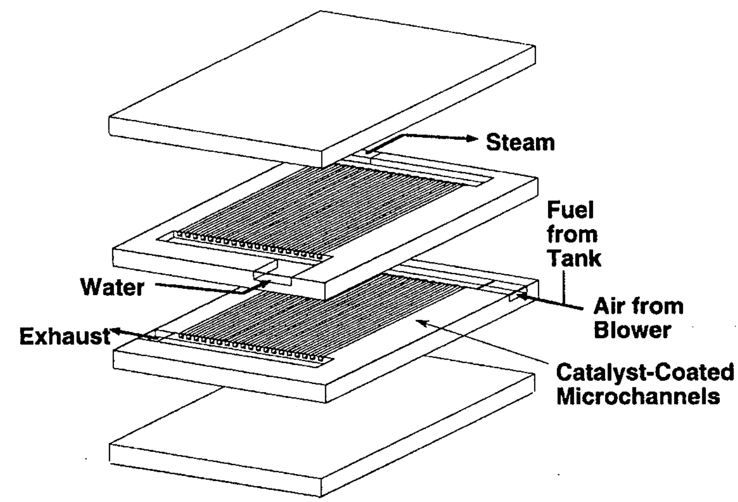

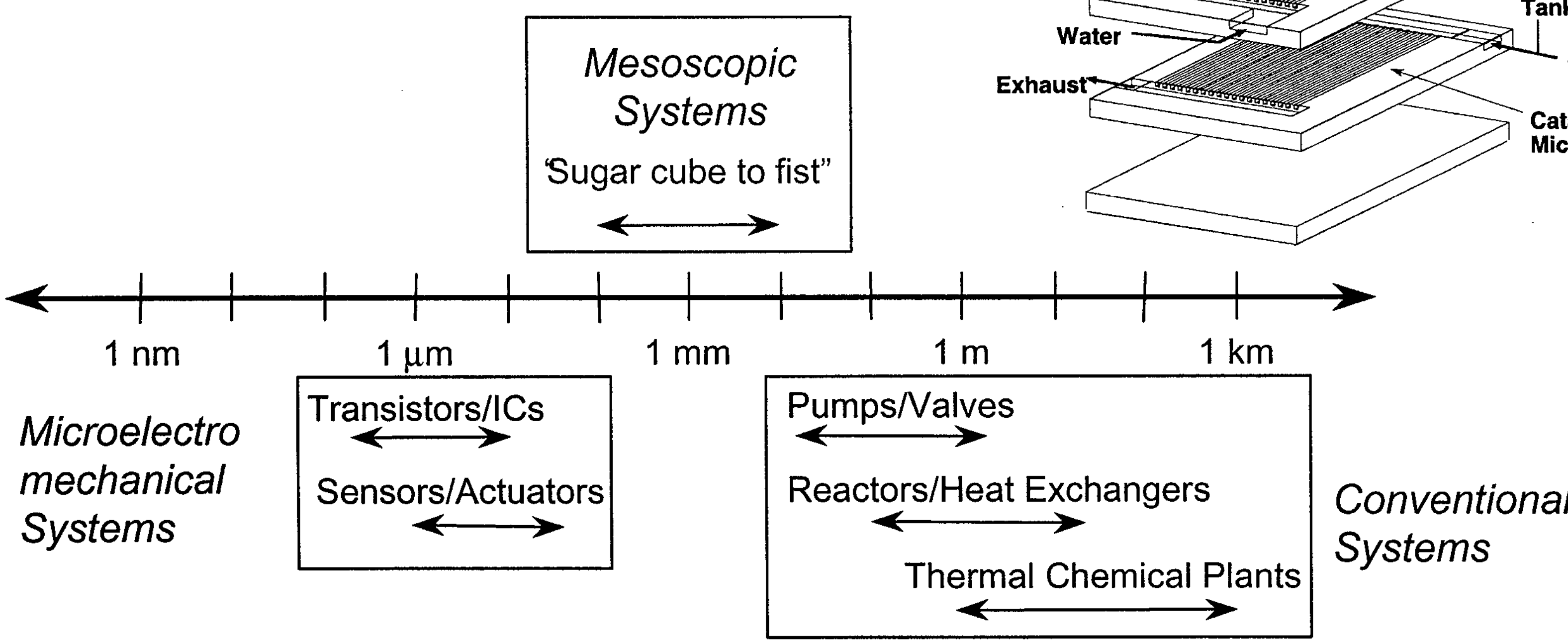

Why a Mesoscopic Machine?

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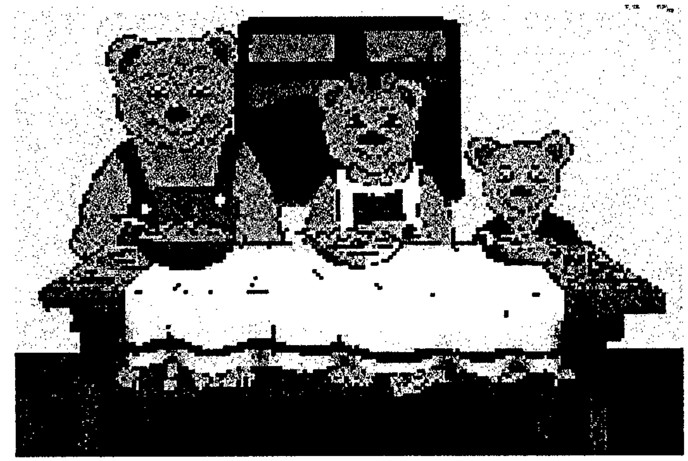
Unique opportunities by bridging the size range between conventional machines and MEMS

- **Enhanced heat, mass and momentum transport**
- **Optimal size range for a wide variety of chemical reactions and fluidic functions**
  - » **Larger:** difficult to accurately control surface chemistry, heat and fluid flows
  - » **Smaller:** dominance of thermal and fluidic properties by wall interactions => high pressure drop, low throughput

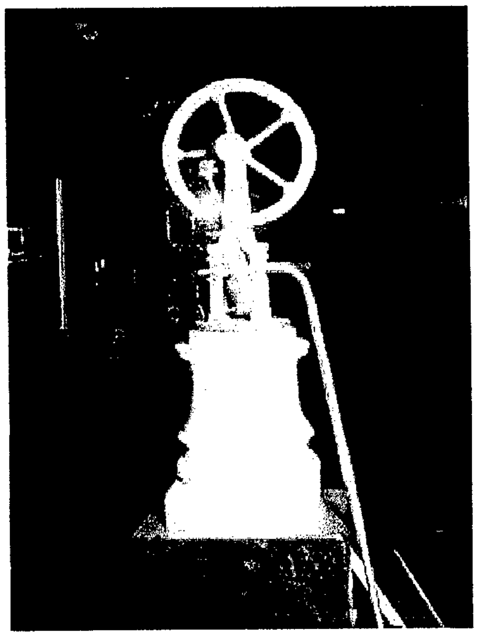


Scaling laws can be used advantageously to replace larger machines

- **Multiple, smaller machines operating in parallel**
- **Greater system reliability**
- **Minimize mass, power, materials, and manufacturing costs while maintaining the performance of larger systems**

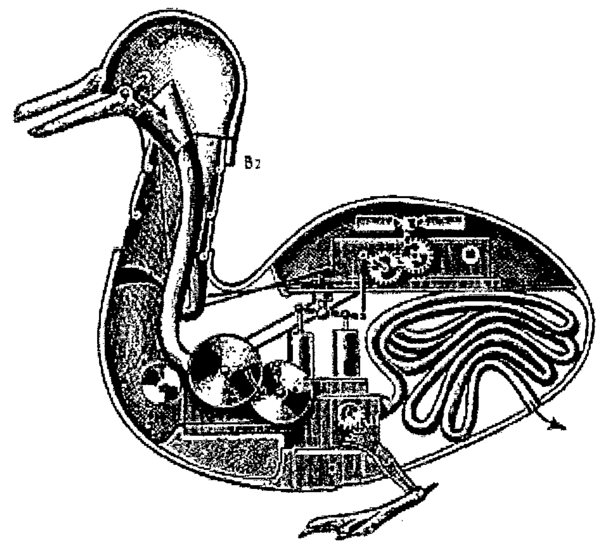
Meso-Machines are *NOT* New!!

Miniature Steam Engine
Benjamin Warner (1845)



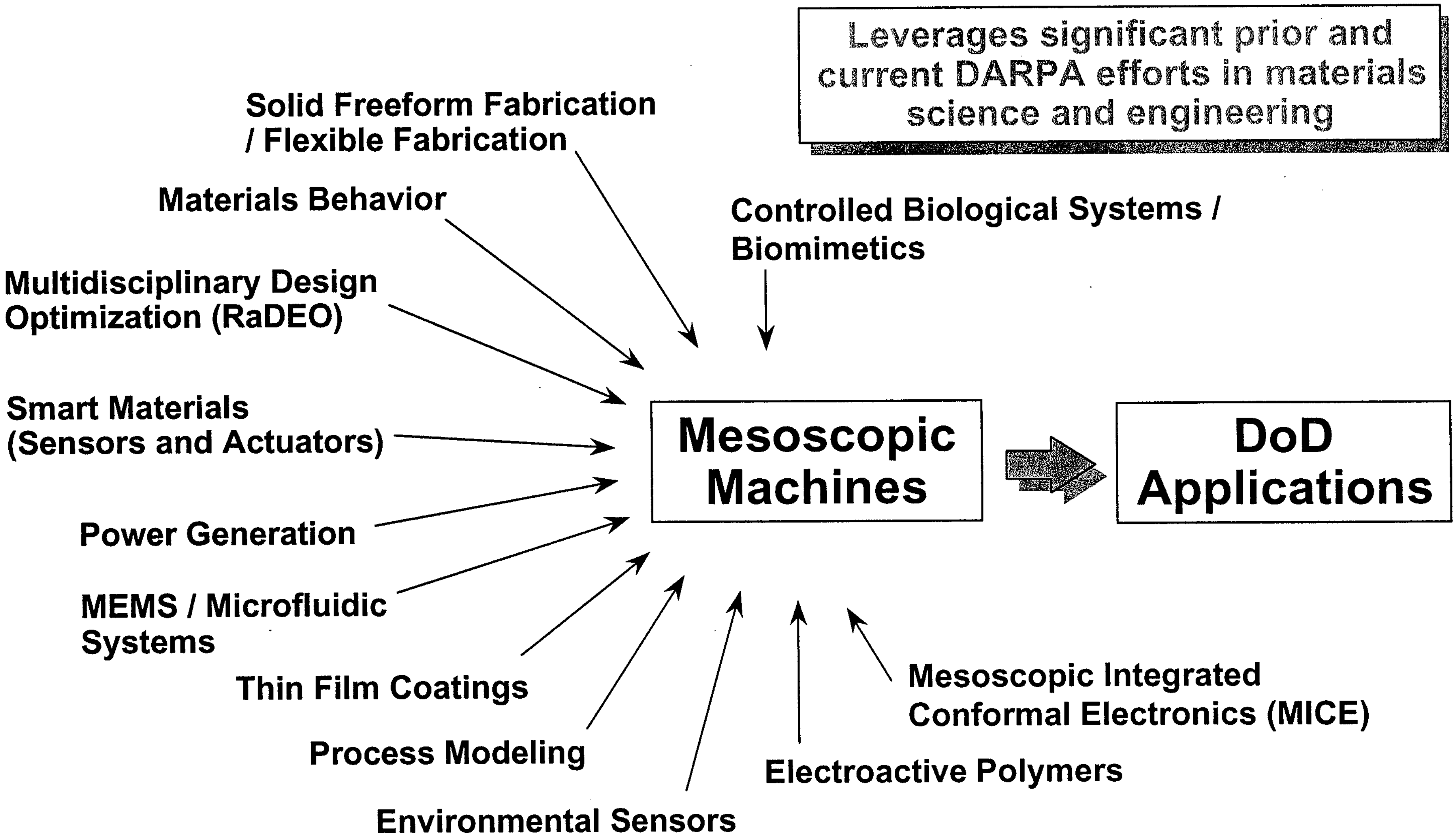
1"x 1"x 2"
1/16"bore, 3/8"stroke

Autonomous Biobot
Jacques de Vaucanson (1700s)



>1000 mechanical parts
ate, extracted energy, excreted waste

Mesoscale Machines: Technical Building Blocks



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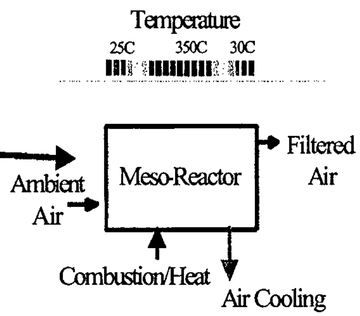
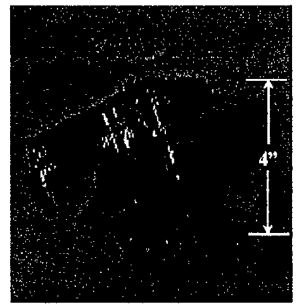
Meso-Machines - Enabling Machines for the Warfighter

Air Purification/MesoSystems Inc.

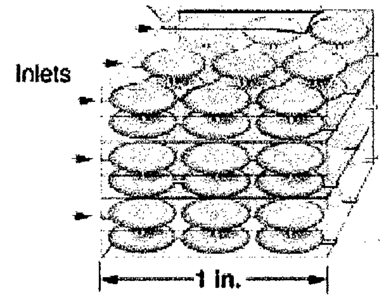


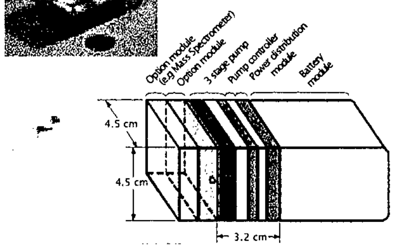
Nanosats/LANL



BWD Detection Pumps

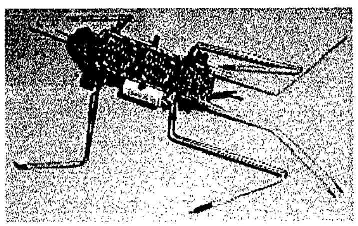
Honeywell SARCOS

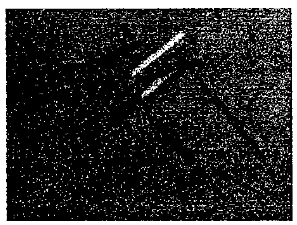


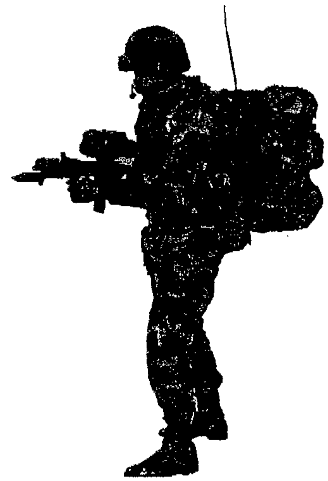


Situational Awareness

LANL Vanderbilt

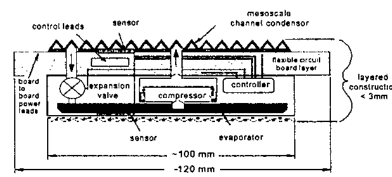


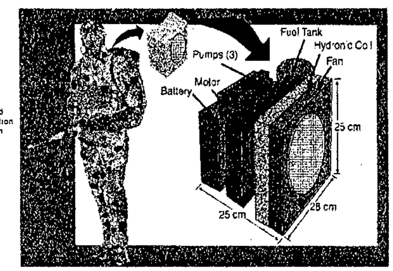




Cool Uniforms

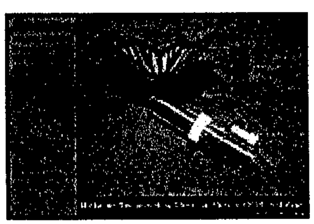
UIUC Battelle/PNNL

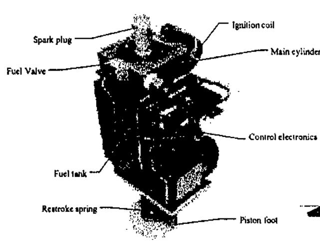




All "terrain" machines

GTRI Sandia

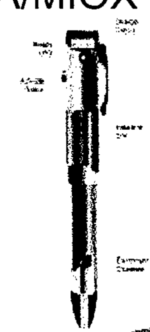




Communication "credit card" GPS

Water Purification

MesoSystems LATA/MIOX Corp.



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Mesoscopic Machines
Technical Issues

- **Device design/scaling laws for fluids, chemistry, combustion, etc.**
  - Absolute size
  - Surface to volume ratio
  - Viscosity, surface tension, and capillary forces
  - Innovative design taking advantage of mesoscale properties

- **Fabrication of "true" 3-dimensional shapes and structures**
  - Complex shapes, integrated structures, attachment, joining, bonding
  - "Conventional" machining (e.g., molding, cutting, stamping, etc.)
  - Additive vs. Subtractive processes (or both)
  - Solid freeform/laminated object manufacturing
  - Lithography/deposition/etching (e.g., MEMS) or LIGA
  - Micromachining, surface finish, warpage
  - Component assembly and packaging
  - Prototyping vs. cost effective manufacturing

Mesoscopic Machines
Technical Issues (cont.)

- **Materials and materials properties**
  - Materials choice and microstructural control
  - Mixed materials and materials compatibility (e.g., electrochemical corrosion, differential thermal expansion)
  - Stress rupture, fatigue, wear, erosion
  - Friction, lubrication and viscous drag
  - Heat and mass transfer, long term diffusion, oxidation, chemical changes

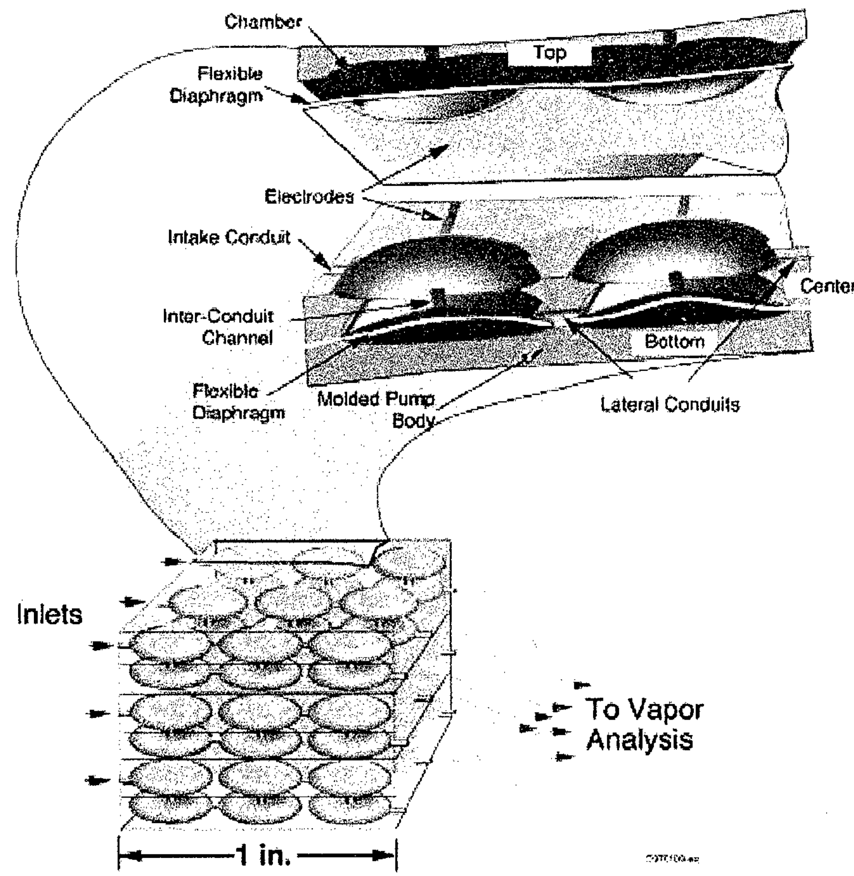
- **Systems vs. Components**
  - Active vs. passive devices (solid state vs. mechanical drivers)
  - System architecture
  - Embedded actuators, electronics, and/or control systems
  - Transduction of electrical to mechanical motion (and visa versa)
  - Reliability

Bistable Electrostatically Activated Mesoscopic Pumping

Honeywell

Electrostatic actuation is *ideal* at the meso-scale
• *Macro* - distances are too large (breakdown of air or fluids)
• *Micro* - nl to μl (too small for "real" work)

- An array of 3 x 30 channels working in parallel can produce pumping rates of more than 10 l/min.
- Series connectability yields higher pressures
- Parallel connectability yields higher throughput
- Highly regular structure makes for easy manufacture
- Pump attributes
  - 1/2 ounce
  - 1 in^3
  - 2 Watts (~25 mA @ 70V)



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Efficiency of an Electrostatic Pumping Channel is Optimized in the *Meso*-Regime

Honeywell Technology Center

$$Efficiency = \frac{\underline{rate\ x\ pressure}}{power} = \left(\frac{V \times \Delta p}{P_d}\right)_{channel} = \frac{fV_0(U-U_{min})^2}{\sqrt{D}fC_0U^2};$$

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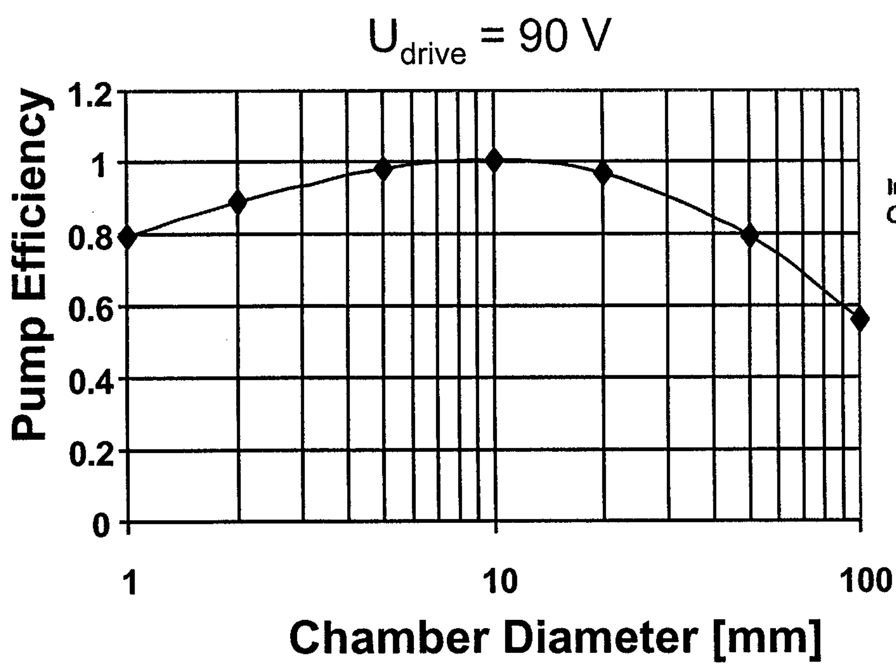
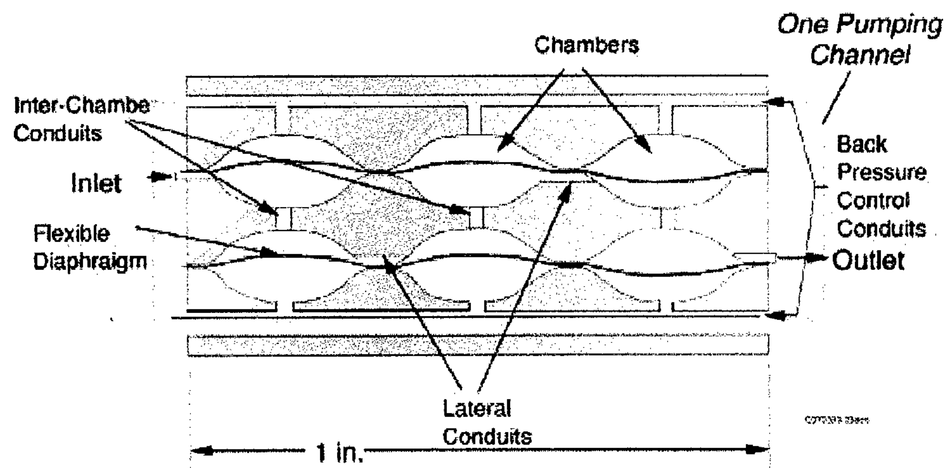
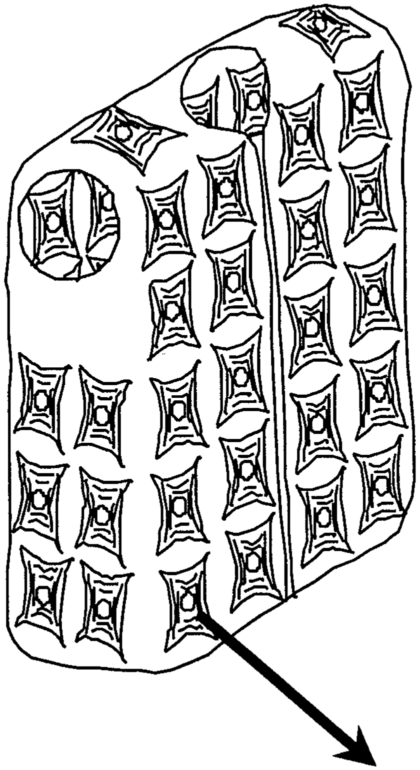


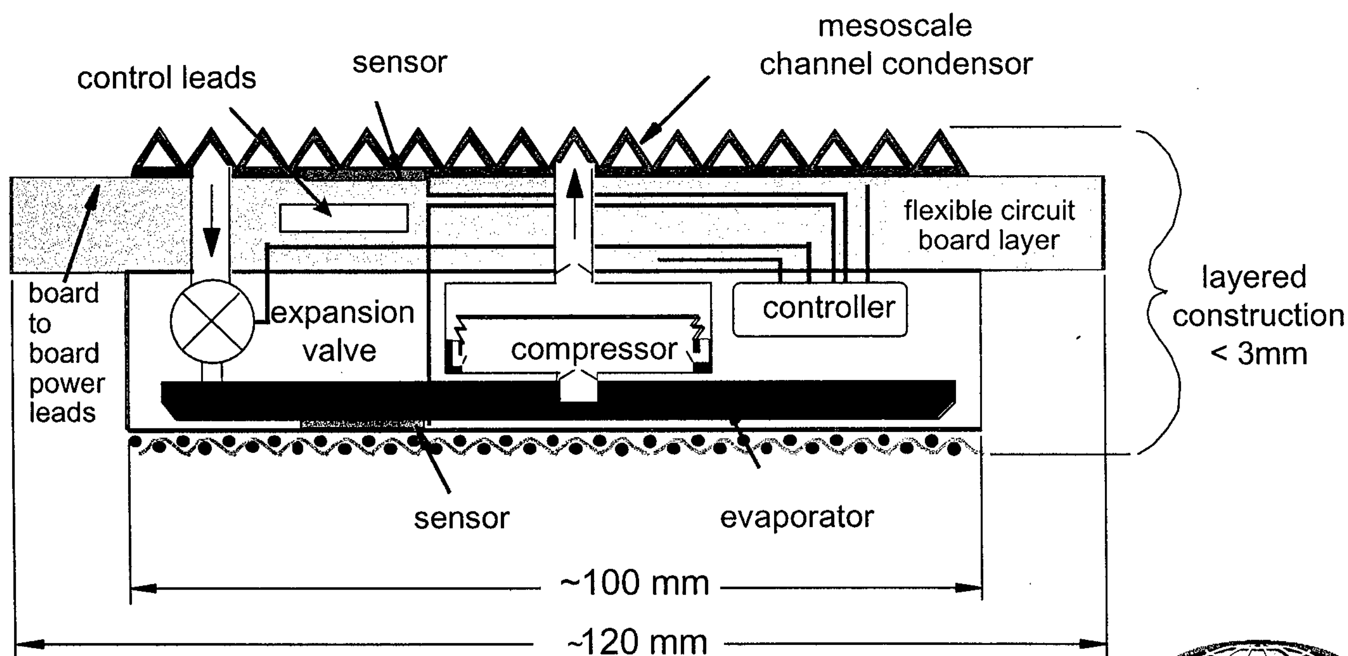


Defense Sciences Office

Electrostatic Meso-Cooler

- 1/3 weight of conventional system
- High COP (~4)
- Q_{in} large because of high surface area
  channels in parallel
- Compressor design -
  low power (0.25 - 1.0 W) electrostatic
  good flow rates
  high compression ratio (4 atm)





University of Illinois

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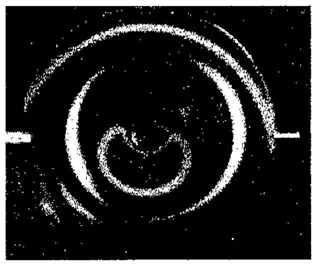
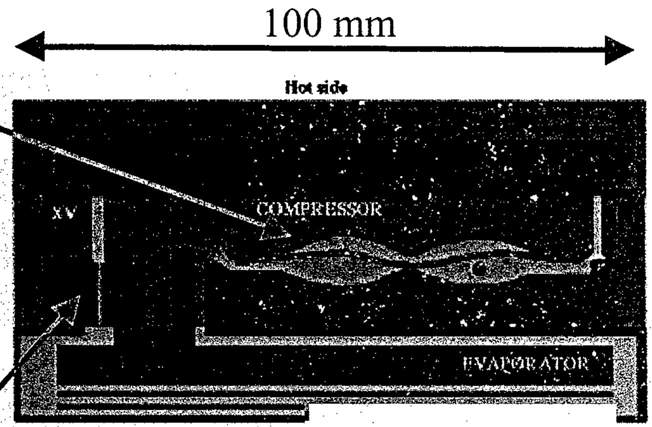
High COP, Light-Weight Electrostatic *Meso*-Cooler

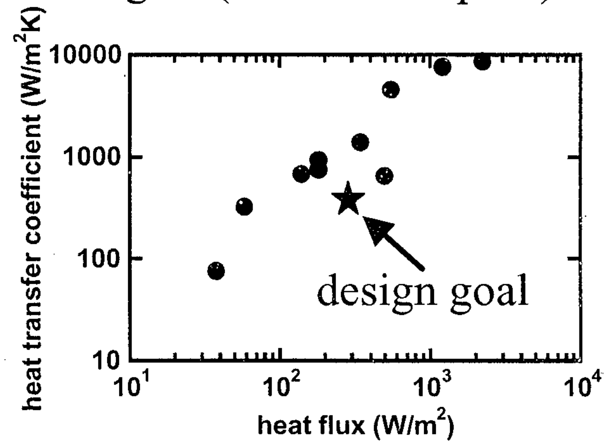
University of Illinois at Urbana-Champaign

Surface roughness ~ 1 nm (better than specs)

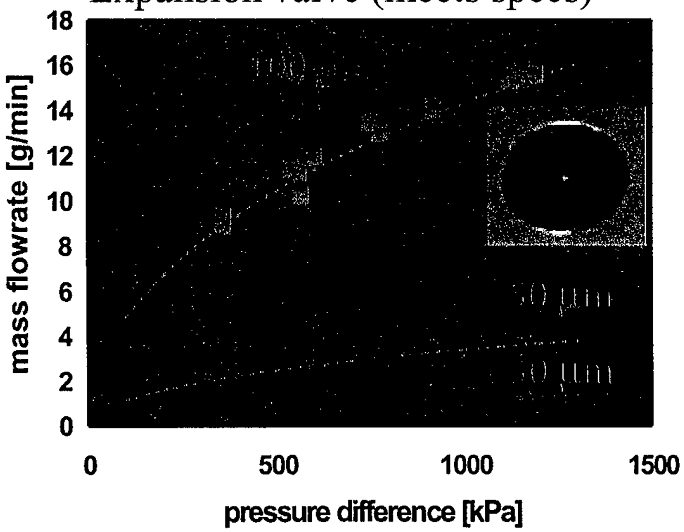


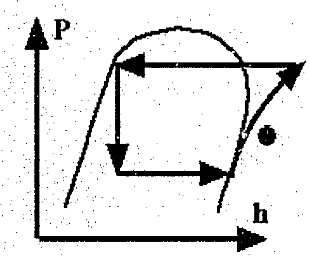


Heat exchangers (better than specs)



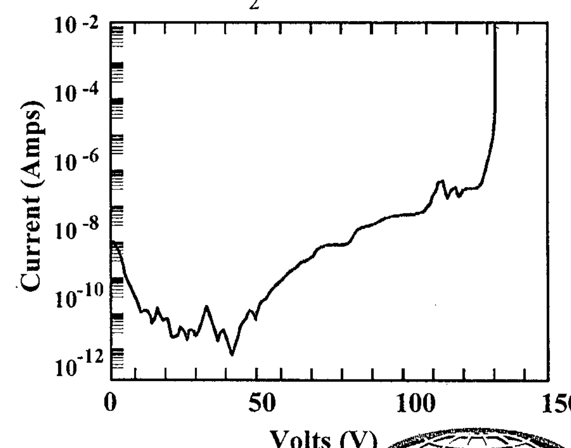
Expansion valve (meets specs)





Excellent dielectric strength (compressor)

$n^+/SiO_2/PI/Cr/Al/Cr/PI$



Water Purification

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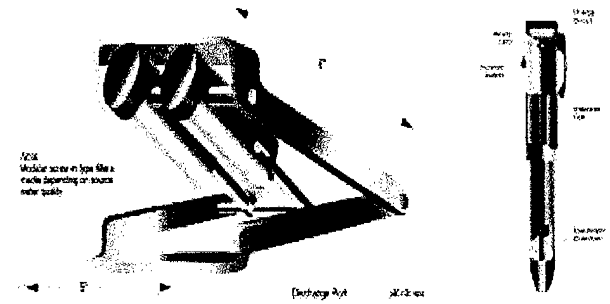
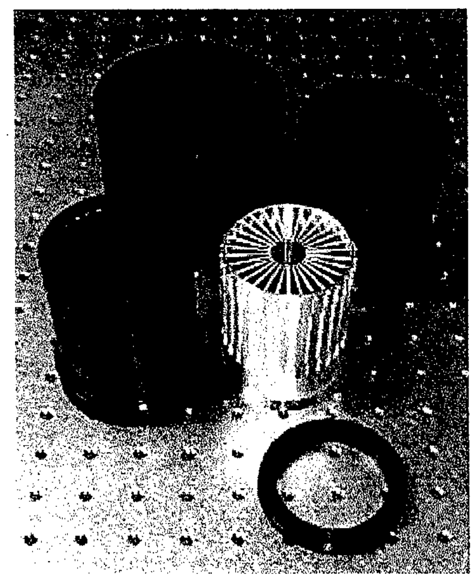
Goal: enable the individual soldier to treat any water source on the spot

- Desalinization from brackish and sea water
- Purify chemically or biologically contaminated water
- System weight < 2 lbs
- System compatible with standard canteen
- Purify water above 32°F
- Provide 1 liter of potable water in 5 minutes
- Provide 12 liters of water/day for 7 days
- Provide 360 liters of water before filter/component replacement

Pulsed harmonic reverse osmosis



Distillation



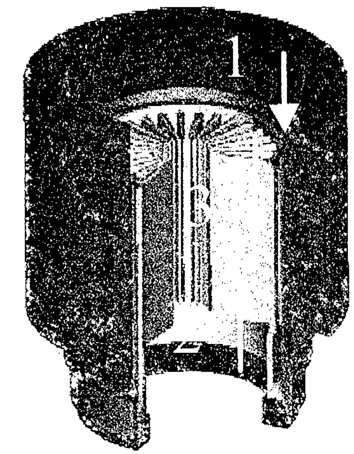
Water Distillation in the Size of Coffee Mug

MesoSystems

Concentric cylinders are clever

- Combustor/boiler/secondary boiler/condenser
- MSR stove (hot part) is inside the cylinder
- Ease of manufacture
- Condenser has thelargest surface area to reject heat

seawater 0.35% NaCl | distilled water ~ 0% NaCl



Preliminary (Final) Attributes:

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- Size ~ 750 cm^3
- Weight ~ 0.5 kg
- Fuel = white gas (diesel) with no batteries
- 0.3 liter/5 min (1 liter/5 min)
- Water/fuel ratio ~ 14:1 (> 25:1)
- Desalinization of seawater with NO fouling
  - water rejection rate 20% (10%)
- Output water 70°C (25° < T < 50°C)

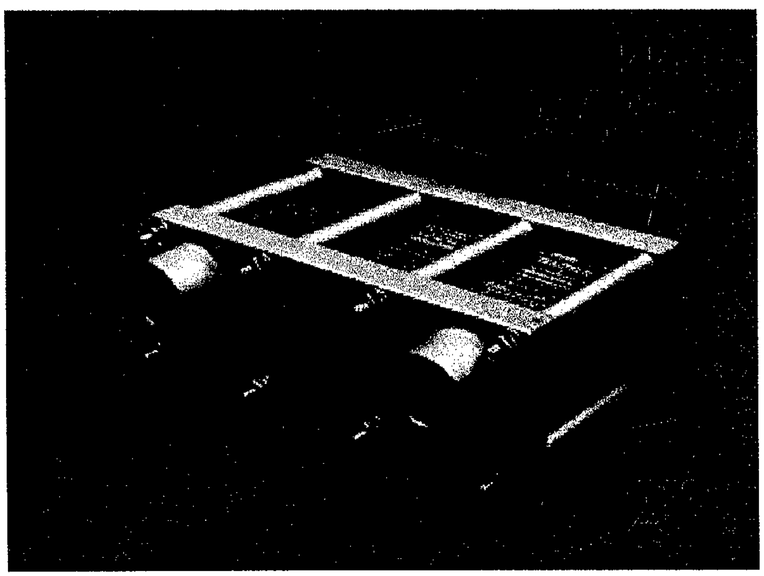
Microbe species	Removal/Destruction Efficiency
Pseudomonas Aeruginosa	> 99.9995%$^+$
Burkholderia cepacia	99.999%
Escherichia coli	99.999%$^{++}$
Generic coliforms	> 99.99%$^+$
Listeria innocua Seeliger	> 99.9995%$^+$
Saccharomyces cerevisiae	> 99.9997%$^+$
Cryptosporidium parvum	> 99%$^+$
Giardia lamblia	> 99%$^+$
Enterovirus	> 99%$^+$
BG spores	> 99.8%$^+$

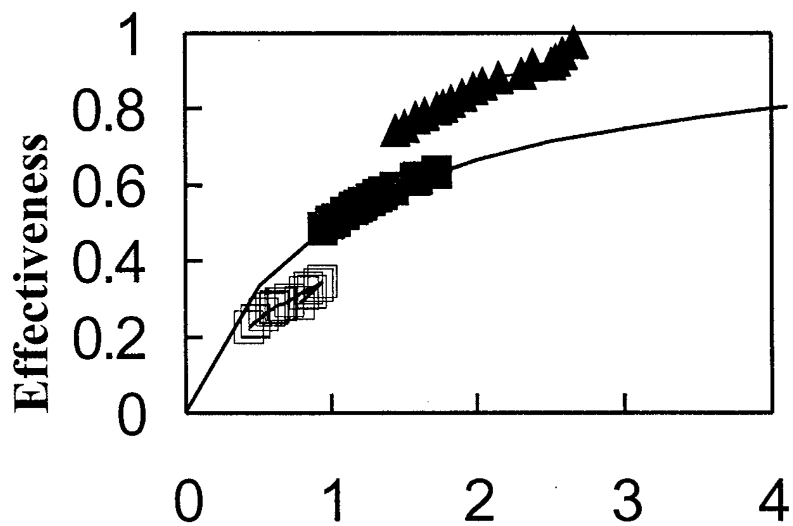
$^+$ no organisms observed, limited by detection limit
$^{++}$ similar concentration to raw sewage
Concentrations used were 10^5 - 10^6x normal conditions

Necessity is the Mother of Invention and *Meso* Is Happy to Participate!

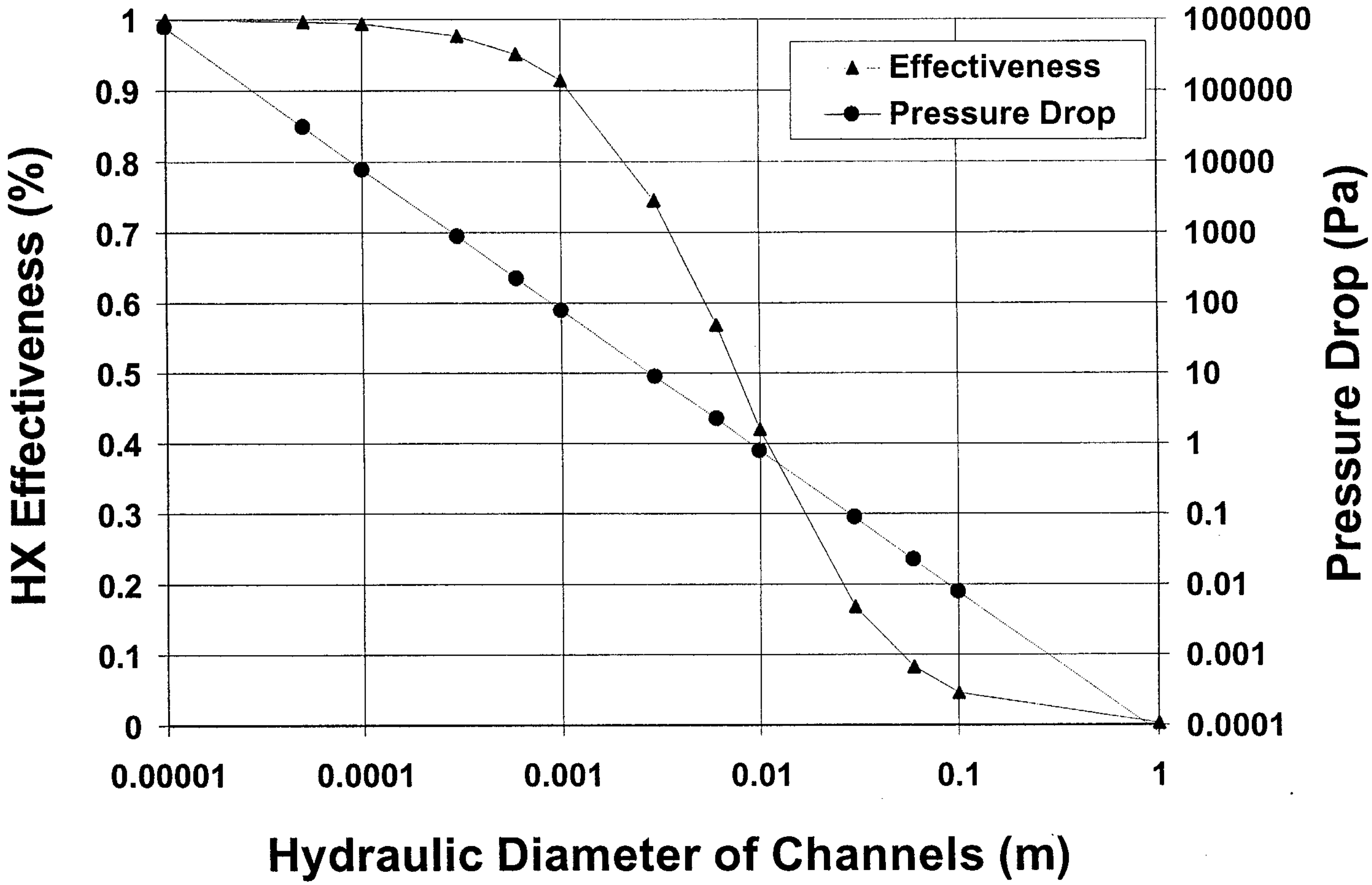
Phenomenal Meso-Heat Exchangers

- Macro-heat exchangers - 20-30% efficient
- Program start: *meso*-heat exchangers - 50-60% efficient
- Newest *meso*-heat exchangers - 96% efficient





We Need Good Heat Exchangers With Low Pressure Drops: Does Size Matter?



MesoSystems

Defense Sciences Office

DARPA

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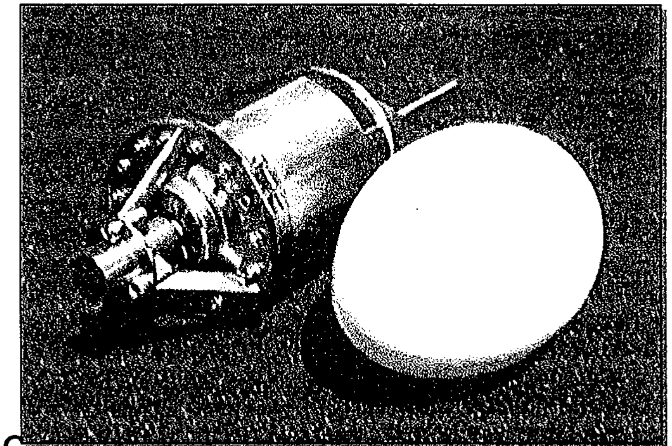
Mesoscale Turbine Engines

M-Dot, Inc.

Gas Turbine Driven, Electric Power Generator



Quiet … … … … …. . Field deployable

Powerful … … …. .. 1 kW class/1.3hp

Portable … … .... Less than 1 kg

Miniature … … … The size of a large egg

Efficient …. … … 3 hr on a liter of heavy fuel

Robust …. … … … . Multi-fuel/low maintenance

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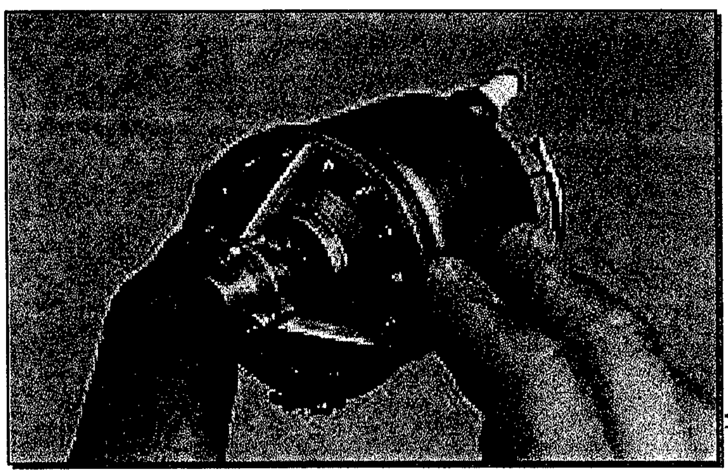
Status

- Engine spun under its own power at speeds up to 311,000 rpm
- Bearing design and fabrication issues

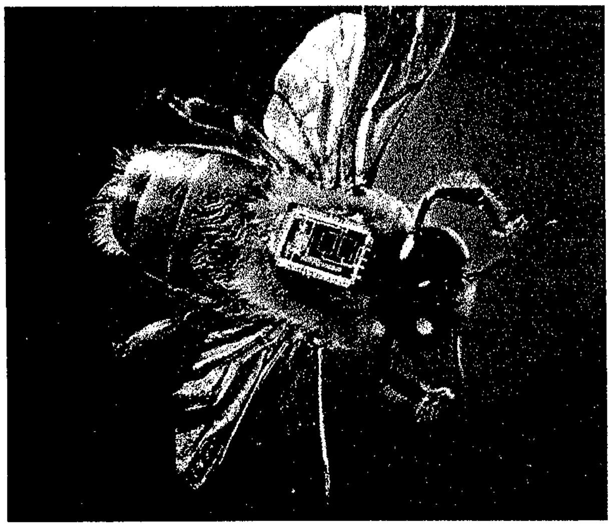


Spinoffs

- 452,000 rpm ultra high speed electric motor
- Mesoscopic refrigeration & cryo compressors
- Mesoscopic refrigeration blow-down turbines
- Complete, self-powered, refrigeration systems
- Mesoscopic heat & power co-generation systems

Animal Locomotion: *Biological Inspiration Toward the Design of New Meso-Robots*

Robert Full, Department of Integrative Biology, UC Berkeley



Oak Ridge National Laboratory

Mesoscopic Animals -

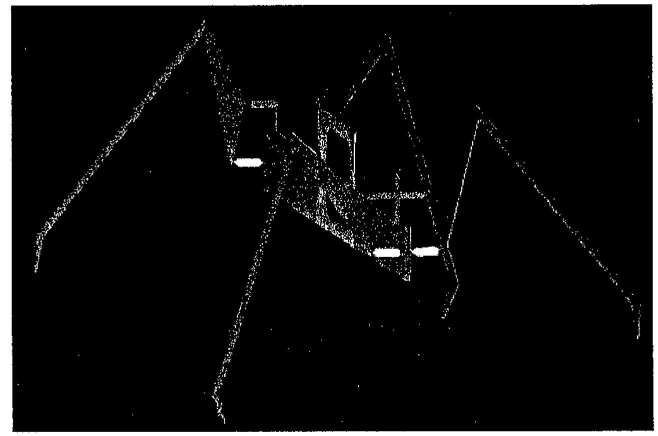
- Multi-legged - *high stability and high maneuverability*
- Inertia / Gravity - *dynamic similarity*
- Speed / Length - *high*
- Efficiency - *low*
- Force and Strength / Weight - *high*
- Surface Tension / Weight - *high*
- Inertia / Viscous - *intermediate*
- Power / Weight - *high*

Single Actuation Schemes for Mesoscopic Robotic Motion

Vanderbilt University

The structure *is* the actuator

- Motion by exciting skeletal structure at the appropriate frequency
- Use different resonant frequencies to control direction of motion
- Optimize design and performance of robotic bugs



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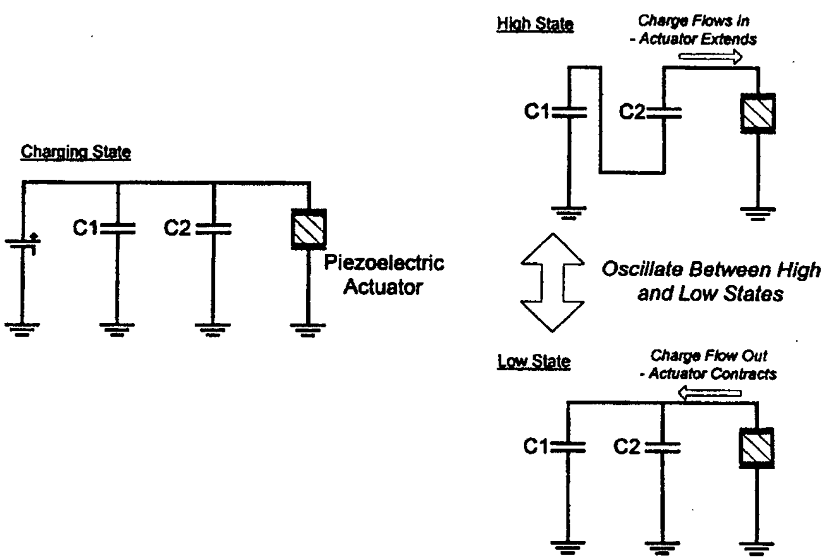
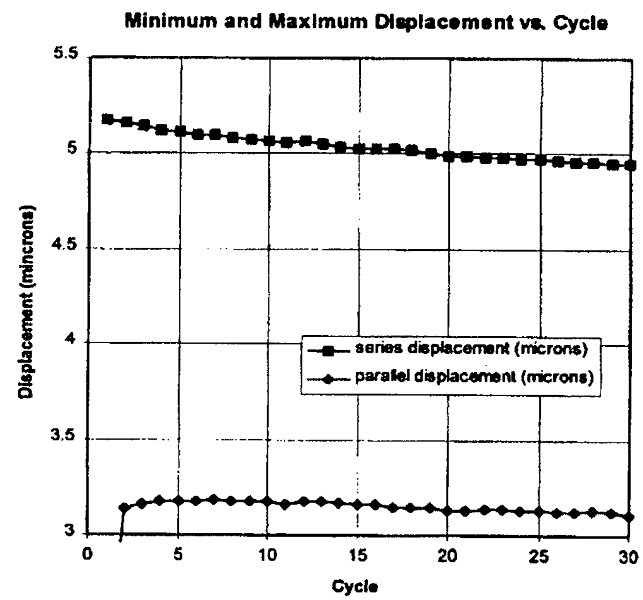
Novel recoverable energy storage scheme using piezoelectric actuators





Shape Deposition Manufacturing (SDM) Process Sequence

Stanford U., Carnegie Mellon U., ACR Inc.

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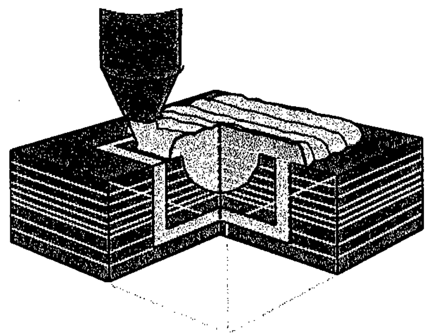
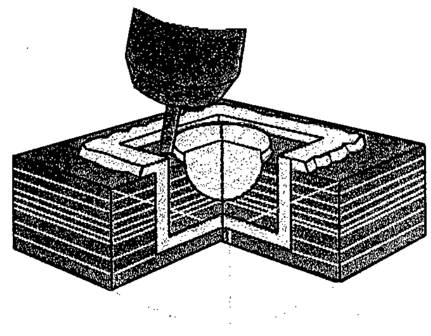
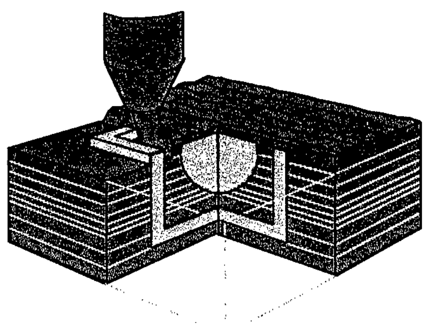
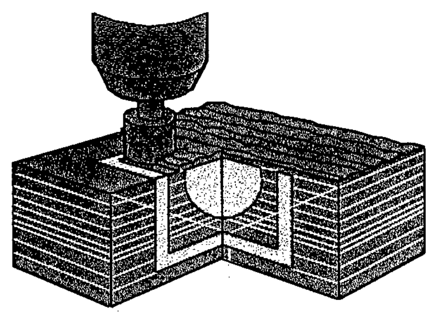

1. Deposit Part Material


2. Shape Part Material


3. Deposit Support Material


4. Plane Support Material

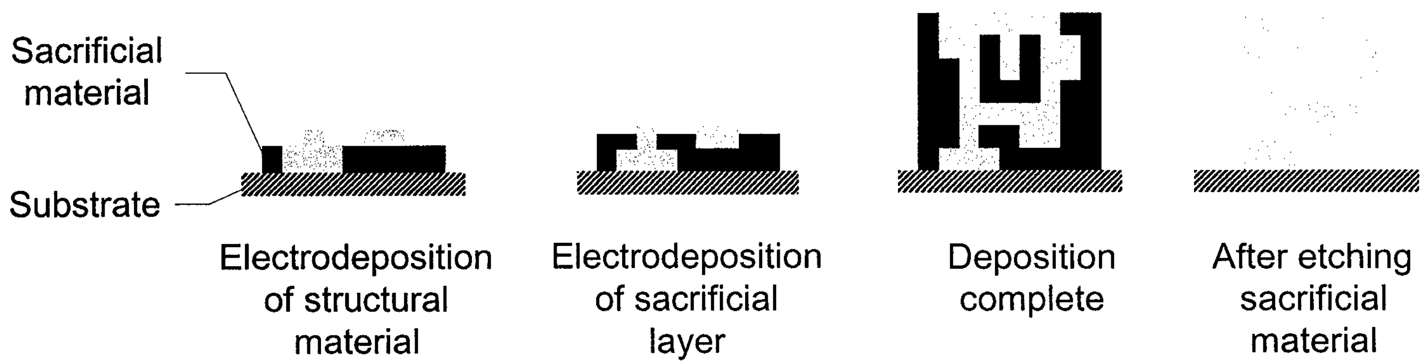
Surface Finish: 0.00075 - 0.001 mm (30 - 40 micro inch)

Tolerance: <0.001 inch

Build Rate: 3 - 20 mm/hr over 250 mm x 250 mm (will be increased by ~30% with air-jet cooling

Meso-Scale Electrochemical Fabrication (EFAB)

ISI/University of Southern California



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CMOS compatible

Fast: 3x less steps than conventional masking

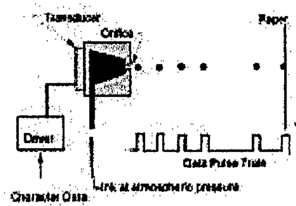
Application driving tool development:

- ground motion sensor
- solenoid actuator (spring)
- power supply
- gesture recognition

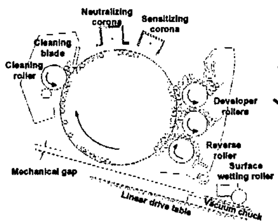
High resolution: 25 micron feature definition with 'Instant Masking"

Meso-Electronics - *Direct Fabrication of Electronics*

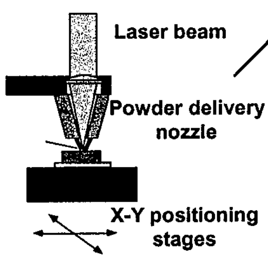
Tools



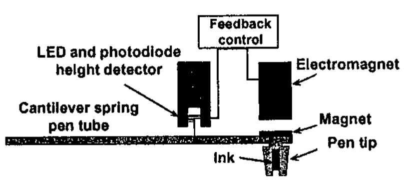
SRI International



Electrox Corp.

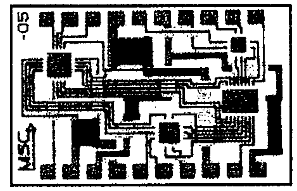


Otpomec Inc.

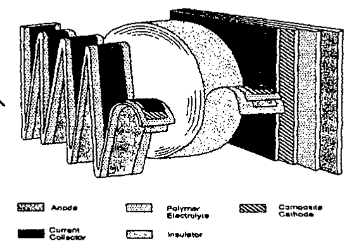


Ohmcraft/Sandia

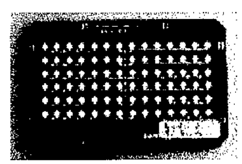
Devices



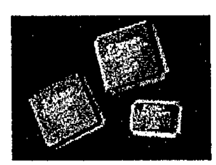
Direct-write passive components & interconnects



Direct-write batteries



Direct-write high gain antenna



ICs*

'Credit card"GPS

- Volume: x18 smaller
- Weight: x5 less
- 75% fewer process steps
- Structure fabricated on complex geometries
- Variety of materials
- Performance advantage

*Thinned ICs will not be fabricated by meso-electronics - they will be commercial

Direct-Write Passive Components

Potomac Photonics Inc./Naval Research Laboratory

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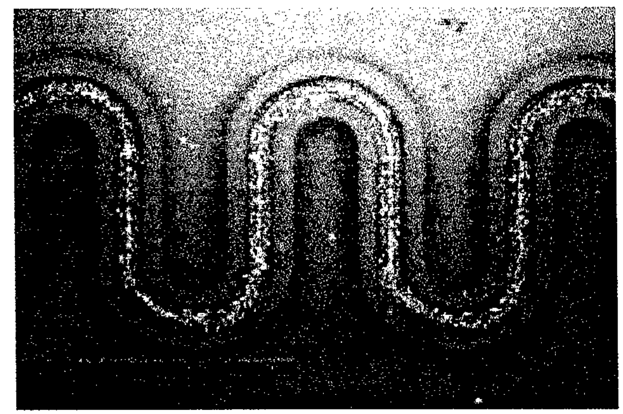
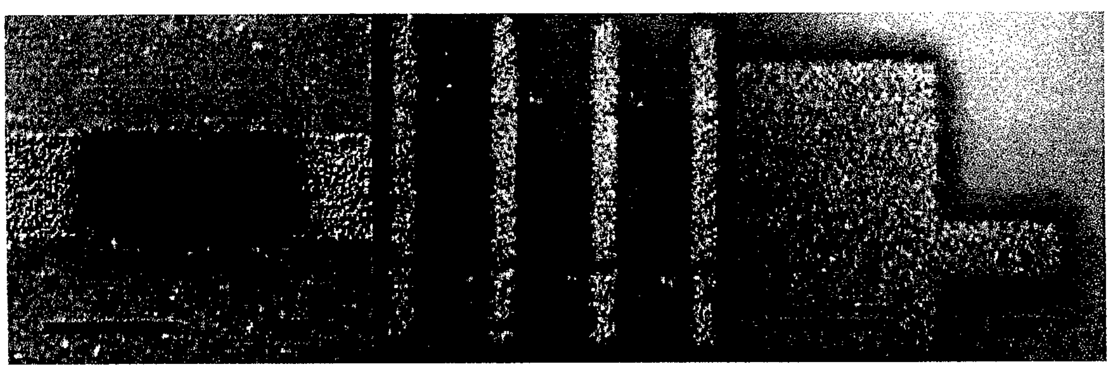
- 3-D fabrication
- *in situ* trimming
- Room temperature deposition
- Works with any material/substrate
- Conformal
- No solder!

30 mm Au lines



Resistors Inductors Capacitors



The DARPA Program: *Exploit Physics at the Mesoscale for the Individual Warfighter*

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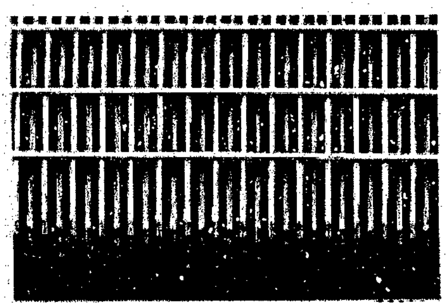
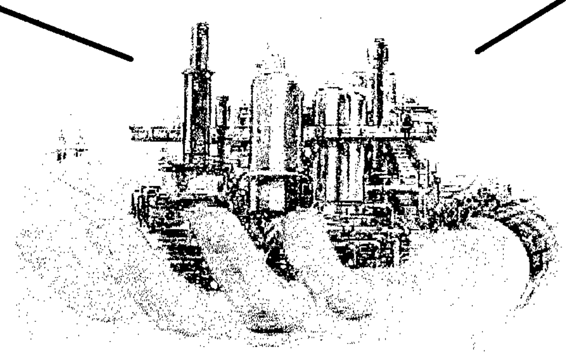
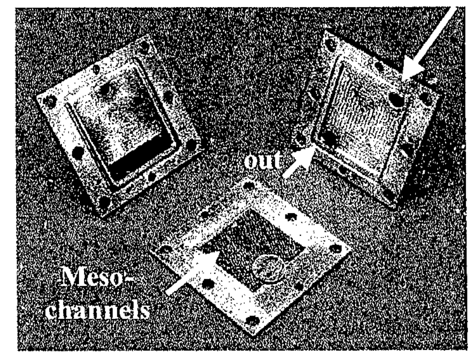
Optimum size for chemistry (combustion)
air/water purification, cooling, engines

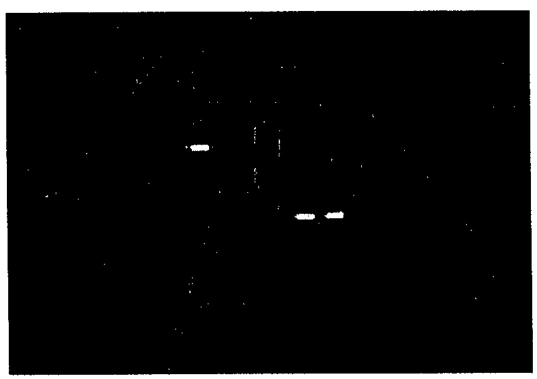




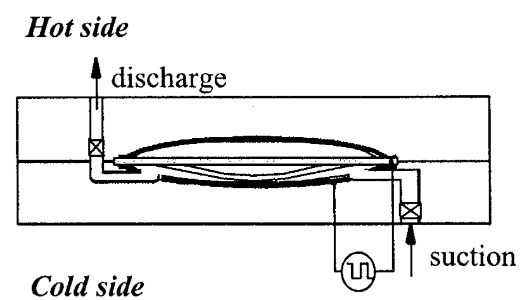
Optimum size for heat transfer
air/water purification, cooling, engines



Energy efficient structural resonance
robots, water purification, flying



Optimum size for electrostatic actuation
pumps, cooling, robots



Developing Conducting Polymers for Charge Storage Applications

J G. Killian, Y. Gofer, H. Sarker, J. Giaccai,
T. O. Poehler, and P. C. Searson

Department of Materials Science and Engineering
The Johns Hopkins University
Baltimore, MD 21218

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Motivation

- Conducting polymer electrodes
  - Cheap; easy to process.
  - Improve charge storage properties of electronically conducting polymers through substituents and copolymerization.
  - Develop improved synthetic approaches and alternative processing techniques.

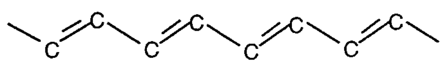
- Electrolyte Development
  - Investigate salt/solvent combinations appropriate for polymer electrode material of choice and processing method.

- Battery Prototype and Testing
  - Develop methods and materials to produce batteries based on conducting polymer technology and incorporating current battery fabrication techniques. Large redox window

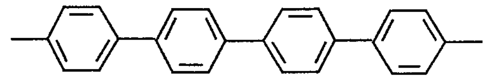
High charge capacity

Low capacity fade

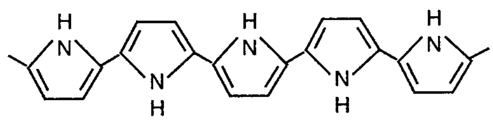
Common Electronically Conducting Polymers



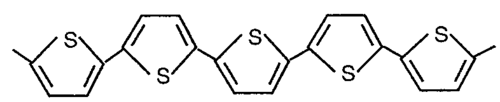
Polyacetylene



Polyparaphenylene



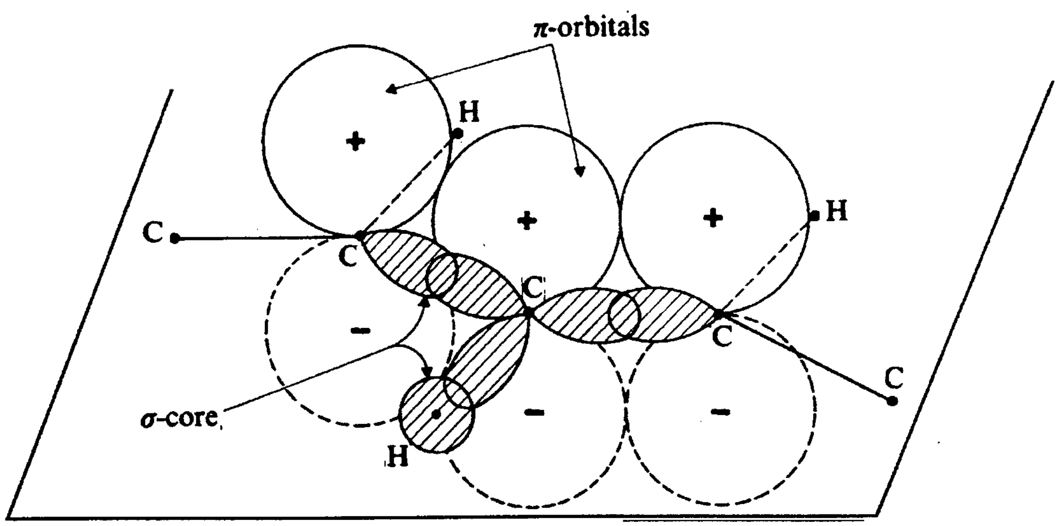
Polypyrrole



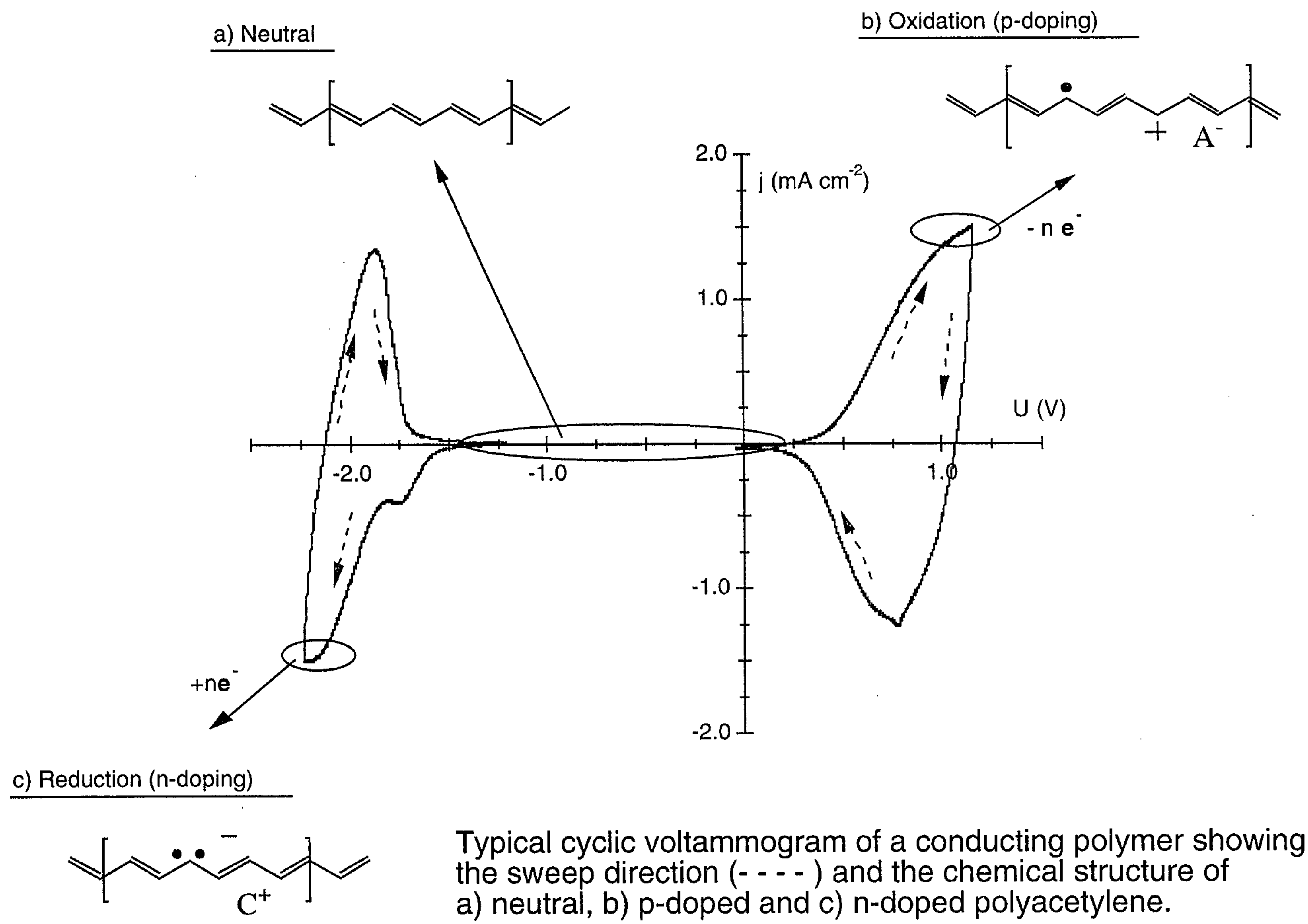
Polythiophene

Features

- •-conjugation
- extended chain length
- planarity
- stereoregularity



Conducting Polymer Electrochemistry

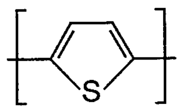


Typical cyclic voltammogram of a conducting polymer showing the sweep direction (- - - -) and the chemical structure of a) neutral, b) p-doped and c) n-doped polyacetylene.

A^- and C^+ represent the counterions.

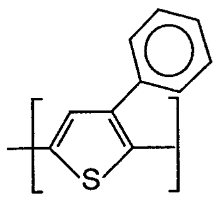
Designing Monomer Structures

Polythiophene



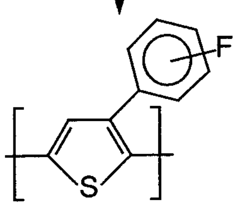
moderate p-doping (-0.16 e/mu)
low n-doping (-0.10 e/mu)

goal: improve doping levels



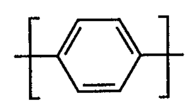
improves p-doping (-0.25 e/mu)
and n-doping (-0.25 e/mu)

goal: control electronic properties



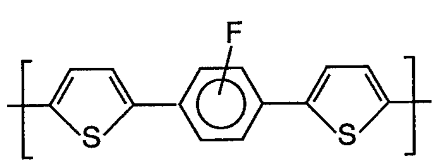
substituent influences n-doping;
no effect on p-doping

Polyparaphenylene



high doping levels
(-0.60 e/mu)

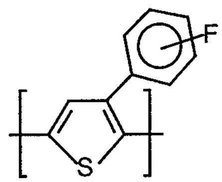
goal: minimize pendant groups
combine into multi-ring monomer

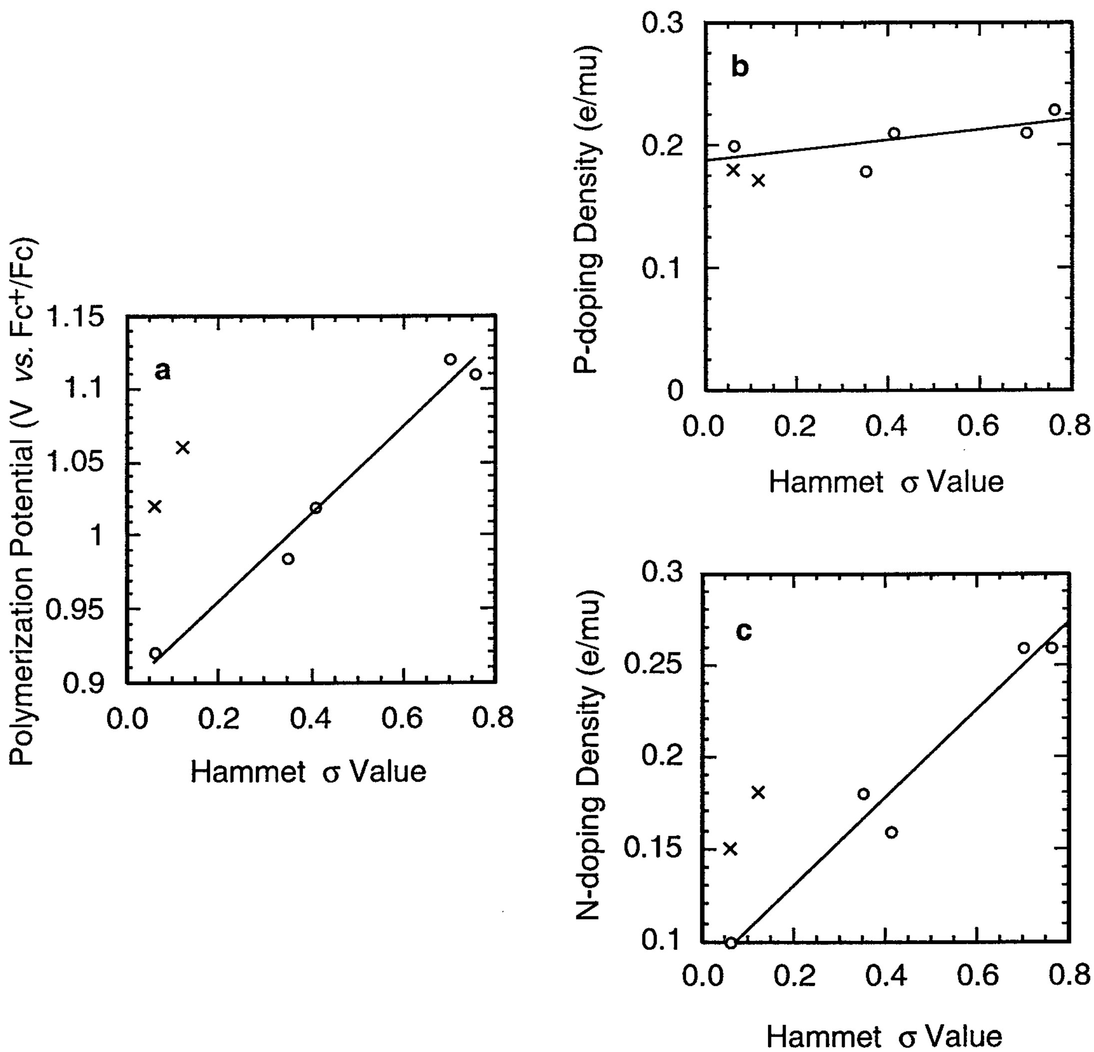


Higher p-doping levels
influenced by substituent
(-0.50 e/mu)

Electronic and Steric Effects of Substituents

- Previous work on polyfluorophenyl thiophenes systematically incorporated F on a pendant phenyl ring to influence the electronic properties.





- Refs.: H. Sarker, et al, *Synth. Met.*, **88**, 179 (1997).
  Y. Gofer, et al, *J. Electroanal. Chem.*, **443**, 103 (1998).

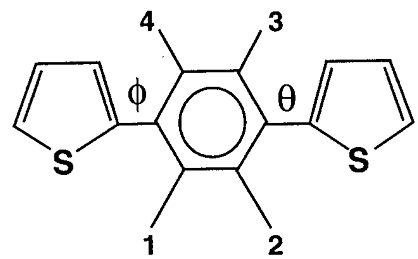
Electrochemical Doping: Fluoro(phenyl-thiophene)'s

polymer	n-doping doping density (e/mu)[a, b]	n-doping charge capacity (mAh g^{-1})[b]	n-doping charge retained over 100 cycles (%)	p-doping doping density (e/mu)[a, b]	p-doping charge capacity (mAh g^{-1})[b]	p-doping charge retained over 100 cycles (%)
p-3,4,5TFPT	0.26	32.1	53	0.23	28.4	90
p-3,5-DFPT	0.26	35.2	37	0.21	29.0	92
p-3,4-DFPT	0.16	21.3	85	0.21	28.5	88
p-2,4-DFPT	0.18	23.9	76	0.17	23.5	91
p-4FPT	0.10	14.8	88	0.20	30.6	87
p-3FPT	0.18	26.8	88	0.18	26.7	87
p-2FPT	0.15	22.6	80	0.18	26.8	94

[a] electrons per monomer unit, [b] first cycle; electrolyte = 0.25 M $TBABF_4$/PC

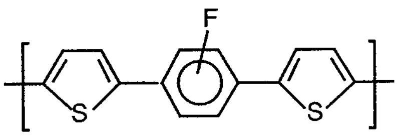
Electronic and Steric Effects of Substituents (cont.)

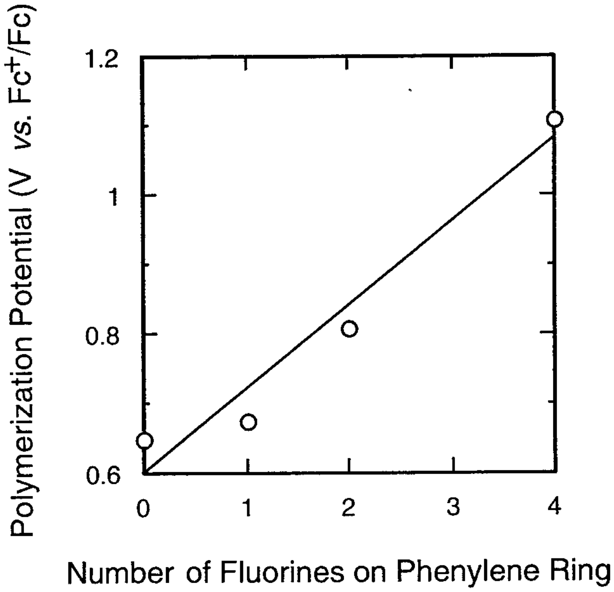
- In multi-ring monomers, both electronic and steric influences of substituents are important.



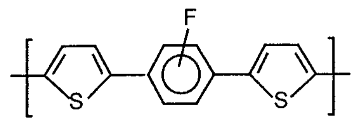
Monomer	Substituent	ϕ (°)	θ (°)
THB	1 = 2 = 3 = 4 = H	36.0	36.0
TFP	1 = 2 = 4 = H, 3 = F	38.0	46.0
T2FP	2 = 4 = H, 1 = 3 = F	46.9	46.9
T4FP	1 = 2 = 3 = 4 = F	89.1	89.1

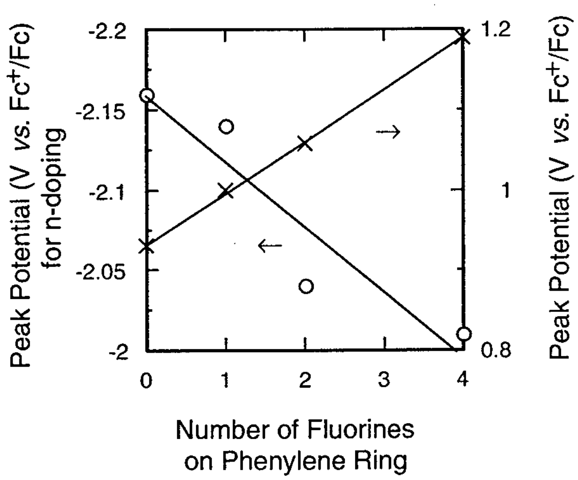
- Fluorine (electronegativity)
- Steric influence (modify •-orbital overlap)

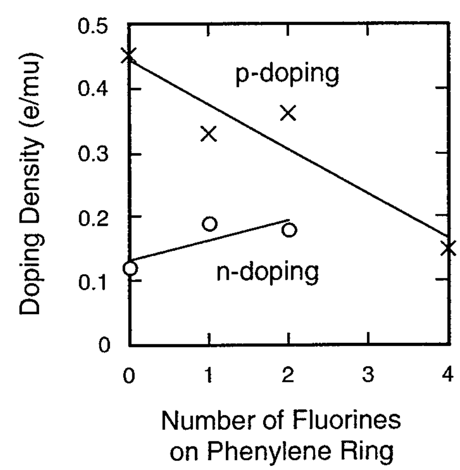

F
S
S


Polymerization Potential (V vs. Fc+/Fc)
1.2
1
0.8
0.6
0
1
2
3
4
Number of Fluorines on Phenylene Ring

Electronic and Steric Effects of Substituents (cont.)







- N-doping: 0.12 - 0.19 e/mu
  (13 - 19 mAh g^{-1})
  U_{peak} → less negative with F
  Capacity → increase with F

- P-doping: 0.15 - 0.45 e/mu
  (13 - 50 mAh g^{-1})
  U_{peak} → more positive with F
  Capacity → decreases with F

- Electronegativity and steric effect of substituents increases the thermodynamic barrier to electron withdrawl and directly influences the polymerization potential and the doping levels.

- Refs.: H. Sarker, et al, *Synth. Met.*, **97**, 1 (1998).
  J. G. Killian, et al, *Chem. Mat.*, to be published.

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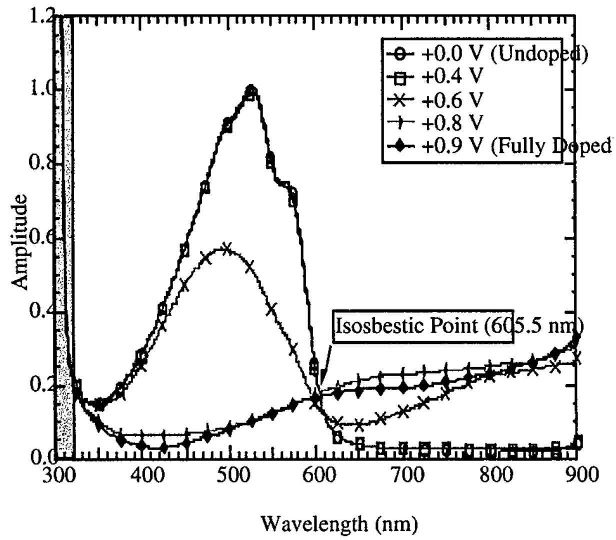
Electrochemical Doping: Fluoro(phenylene-thienyl)'s

polymer	n-doping doping density (e/mu)[a, b]	n-doping charge capacity (mAh g^{-1})[b]	n-doping charge retained over 100 cycles (%)	p-doping doping density (e/mu)[a, b]	p-doping charge capacity (mAh g^{-1})[b]	p-doping charge retained over 100 cycles (%)
pTHB	0.12	13.1	6	0.45	49.4	70
pTFP	0.19	19.7	46	0.33	34.4	91
pT2FP	0.18	17.2	30	0.36	34.4	57
pT4FP	-----[c]	-----[c]	-----[c]	0.15	12.9	59

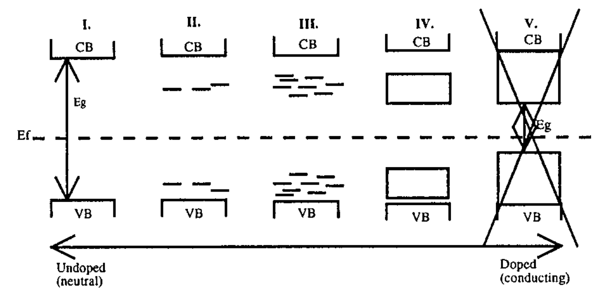
[a] electrons per monomer unit, [b] first cycle, [c] irreversible; electrolyte = 0.25 M $TBABF_4$/PC

Experimental Determination of Band Structure

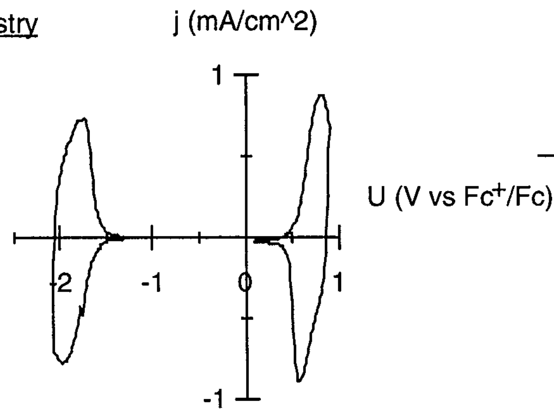
Spectrocscopy



Correlates to
band diagram

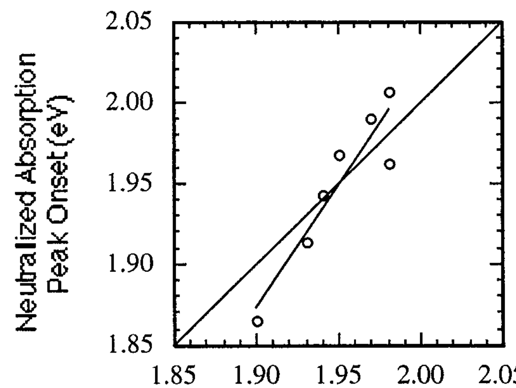


Electrochemistry



Cyclic Voltammetry of p3,4,5-TFPT in PC, SR=25 mV s^{-1}

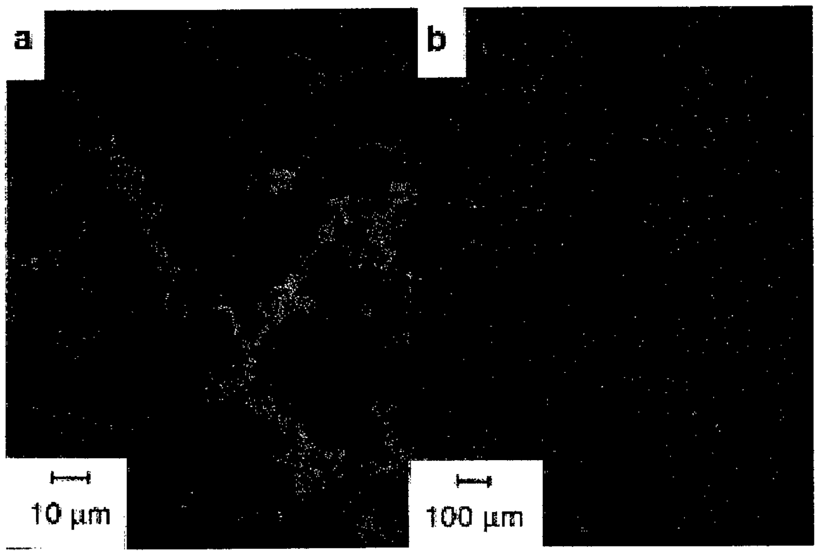
Displays good
experimental
agreement



Difference of Onset Potentials
for N-doping and P-doping (V)

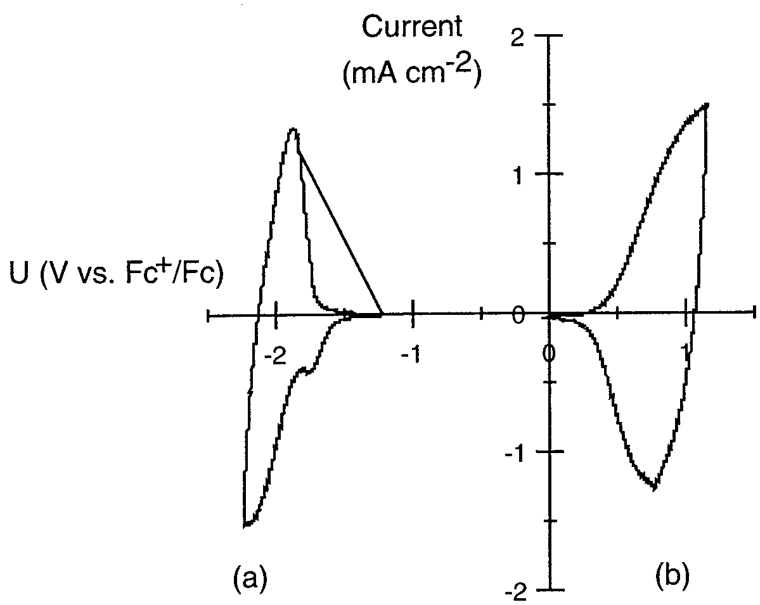
596

Conducting Polymer Film Morphology



Plan view SEM micrographs of an as-deposited pTFPT film electropolymerized on Pt substrates. The images illustrate the continuous nature of the film and the characteristic nodular structure.

Battery Applications: Cell Electrochemistry



For an all polymer battery

- n- and p-dopable material $\rightarrow$ anode and cathode
- high doping density $\rightarrow$ high specific capacity
- maximize ΔU_{peak} $\rightarrow$ high operating voltage

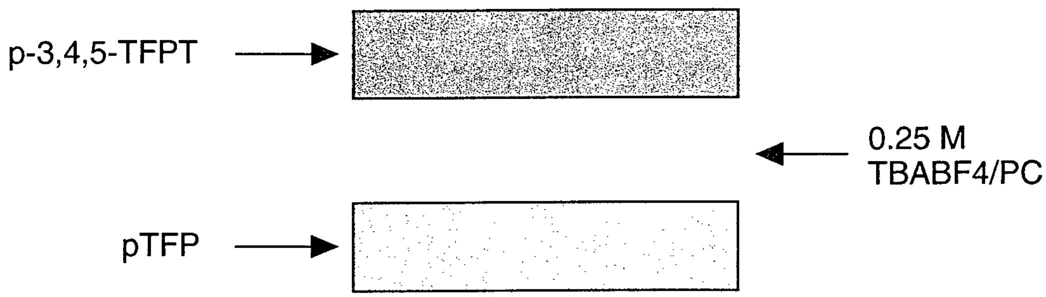
CV conditions: pTFP in 0.25 M $TBABF_4$/PC
$\nu = 25$ mV s^{-1}
d = 5 μm

Electrochemical Doping: Battery Applications

polymer	n-doping doping density (e/mu)[a, b]	n-doping charge capacity (mAh g^{-1})[b]	n-doping charge retained over 100 cycles (%)	p-doping doping density (e/mu)[a, b]	p-doping charge capacity (mAh g^{-1})[b]	p-doping charge retained over 100 cycles (%)
pTFP	0.19	19.7	46	0.33	34.4	91
p-3,4,5-TFPT	0.26	32.1	53	0.23	28.4	90

[a] electrons per monomer unit, [b] first cycle; electrolyte = 0.25 M $TBABF_4$/PC

Battery Applications: Cell Construction



Half Cell Reactions (discharge)

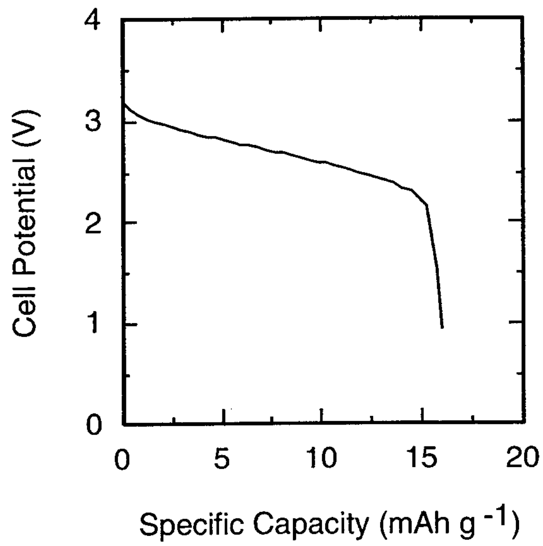
Anode: $[\text{p-3,4,5-TFPT}]^{-} \cdot \text{TBA}^{+} \rightarrow [\text{p-3,4,5-TFPT}]^{0} + \text{TBA}^{+} + e^{-}$

Cathode: $[\text{pTFP}]^{+} \cdot \text{BF}_4^{-} + e^{-} \rightarrow [\text{pTFP}]^{0} + \text{BF}_4^{-}$

Experimental: anode/cathode films - d = 70 μm / 40 μm
charge/discharge @ 250 μA cm^{-2}

Battery Applications: Results and Trends

- 3,4,5-TFPT / 0.25 M $TBABF_4$ + PC / 1Fa-a



Cell Performance

- $V_{average,\ discharge}$ = 2.75 V

  (corresponds to ΔU_{peak} in cyclic voltammetry)

- $V_{maximum}$ = 3.20 V

  (corresponds to ΔU_{max} in cyclic voltammetry)

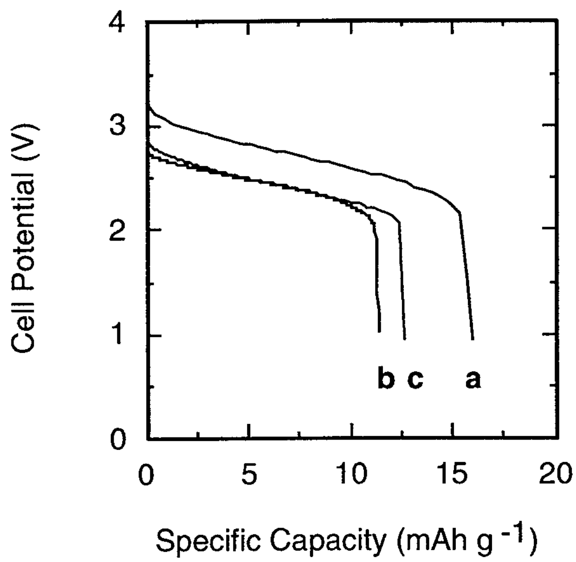
- specific capacity = 16 mAh g^{-1}

  (99% of expected from electrochemistry)

- cycling efficiency = 99.14%

  (lower than expected from electrochemistry)

Battery Applications: Results and Trends



Cell	Maximum Cell Potential (V_{max})	Average Discharge Potential ($V_{average}$)	Specific Capacity ($mAh\ g^{-1}$)	Capacity Fade (% per cycle)
a	3.2	2.75	16.0	0.86
b	2.9	2.5	11.5	0.90
c	2.9	2.6	12.6	0.34

a 3,4,5-TFPT / 0.25 M $TBABF_4$ + PC / 1Fa-a cell

Ref.: J. G. Killian, et al, *Chem. Mat.*, to be published.

b 3,4,5-TFPT / 3.7 wt.% PAN + 0.25 M TBABF4 + PC / 3,5-DFPT

Ref.: Y. Gofer, et al, *Appl. Phys. Lett.*, **71**, 1582 (1997).

c 3,4,5-TFPT / 0.25 M TBABF4 + Sulfolane / 3,4,5-TFPT

Ref.: J. G. Killian, et al, 38th Power Sources Conference, Cherry Hill, NJ, 8 - 11 June (1998).

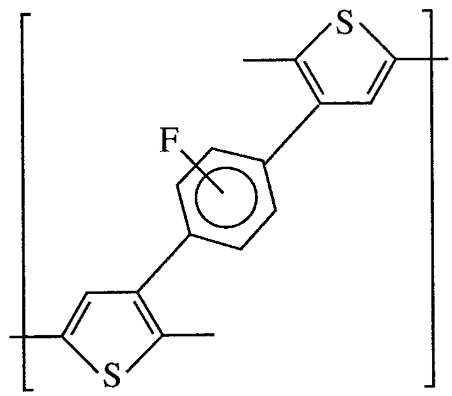
Battery Applications: Results and Trends (cont.)

cell performance can be predicted from

- $V_{average, discharge}$ corresponds to ΔU_{peak} in cyclic voltammetry.
- $V_{maximum}$ corresponds to ΔU_{max} in cyclic voltammetry.
- Specific capacity 95 -99% of that expected from electrochemistry.
- Cycling efficiency is generally lower than that expected from electrochemistry.

Trends in Materials Development

- Improve electronic conduction via a polyfunctional monomer



- Basis for monomer selection:

thiophene moiety → n- and p-dopable

paraphenylene moiety → high doping density

fluorine substituted → influence band gap and doping properties

β–β' linkage → •-conjugated crosslink improve electronic conduction

Conclusions

Materials

- Four series of monomers and corresponding polymers have been designed and synthesized.
- Both chemical and electrochemical polymerization produce electroactive materials.
- Predictable electrochemical properties dependent upon electronic and steric effects of substituents.
- Materials may be reliably characterized by electrochemical and spectroscopic techniques.

Batteries

- Secondary batteries based on conducting polymers have been demonstrated.
- Electrochemistry results translate into battery performance.
- Solvent/electrolyte effects on cell performance are not well understood.

Structure-property relationship and ability to design monomer structure suggest method to improve conducting polymer's electrochemical performance for battery applications.

MICROLAMINATION FOR MICROTECHNOLOGY-BASED ENERGY AND CHEMICAL SYSTEMS

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ABSTRACT

Microlamination is a process for fabricating micro and meso scale systems having intricate arrays of components interconnected within a single block of metal, ceramic, or polymeric material. The process begins by surface machining, or through cutting, individual laminates with patterns containing the desired structure. The laminates are often shims of a base material having desirable mechanical and thermal properties important to the functioning of the final device. Once the patterns are cut, the laminates are surface treated and stacked in a prearranged order. Bonding then takes place forming a single block of material. Some post processing of the block can be performed to dissociate internal structures if needed. This paper describes work being accomplished at Oregon State University on the microlamination process. The paper emphasizes laser micromachining of metal and polymeric laminates. Laser techniques covered include pulsed Nd:YAG-based micromachining at the fundamental and higher harmonics. Also, examples of CO_2 laser machining are presented. Process descriptions are provided and examples given of micro and mesoscale components needed for producing devices useful in the energy, chemical, and biological areas.

INTRODUCTION

Microtechnology-based Energy and Chemical Systems (MECS) are devices that rely on embedded microstructures for their function. The overall size of MECS devices places them in the mesoscopic regime, i.e. in a size range between macro objects such as automobile engines and laboratory vacuum pumps, and the intricate MEMS based sensors that reside on a silicon chip. Thus MECS, although having microfeatures, are large by MEMS standards straddling the size range between the macro- and micro- worlds. These mesoscopic systems are expected to provide a number of important functions where a premium is placed on either mobility, compactness, or point application. The internal processes of these devices rely on length scales that are much smaller than traditional systems. For thermal and chemical applications, a small characteristic size provides the benefits of high rates of heat and mass transfer, large surface-to-volume ratios, and the opportunity of operating at elevated pressures. For other more mechanically operated meso machines such as generators and motors, small dimensions imply rapid response and compact design. Furthermore, these systems can often be volume produced resulting in substantial cost reduction of each device. In the energy area, MECS will find increasingly important uses were small scale heat engines, heat pumps and refrigerators are needed. For example, the development of miniature refrigerators could provide point cooling of high speed electronics and communication equipment for enhancing performance (Little, 1990). Also, power packs based on combustion rather than electrochemistry could extend operating times of electronic devices by a factor of ten (Benson and Ponton, 1993). In the area of chemical processing, miniaturized chemical reactors could provide on-site neutralization of toxic chemicals thereby eliminating the need for transport and burial (Koeneman, et al., 1997). Because many MECS devices rely on fluidic processes, the same technology can be applied to biological applications. Miniaturized bioreactors could provide precisely regulated environments for small groups of cells to enhance their production of therapeutic drugs, or the detection of toxic compounds. Such bio-applications could range from benchtop research to large scale production facilities.

Fabrication techniques developed for IC production have been refined to the extent of supporting a multi-billion dollar industry. Chip manufacturing relies on silicon-based processing where submicron feature size is routinely used in production. MECS do not require the extremely small "line widths" needed to fabricate integrated circuits. Furthermore, for many energy applications, silicon is not the favored base material (Peterson, 1999). It has a much higher thermal conductivity than is desired for energy-based applications and the material, although strong, is brittle, expensive, and cannot always be tailored to specific environmental conditions. Other fabrications techniques (discussed in the next section) have been specifically developed for MEMS. Although many rely heavily on silicon processing (Kovacs, 1998), others can produce very small structures in metals electrodeposited on a surface or within a micromold. Again, for MECS applications, the feature size of these MEMS fabrication techniques are usually much smaller than what is needed for MECS.

Because MECS are fundamentally different than traditional ICs and MEMS, they require different materials and fabrication processes. The fabrication method discussed in this paper is microlamination (see for example, Haas et al., 1993, Haas, 1995, Wegeng et al., 1997, and Young, 1996). Although it has been used in the past, and is currently the basis for producing a commercial product (Anderson, 1989), extending the applicability of the method to MECS is being pursued by only a few groups. The method is based on micro-lamination of metals, ceramics, and polymers. The process begins by

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surface machining, or through cutting, of a single laminate with a pattern containing the desired structure. The laminate is often a shim of a material having desirable mechanical and thermal properties important to the functioning of the final device. Once the pattern is cut, the laminates are surface treated and stacked in a prearranged order. The stack is then bonded together forming a single block of material. For the method to have utility, a machining method capable of fabricating structures in the laminating material is needed. The method must be versatile, easy to use, and capable of rapidly machining (with through-cuts and surface texturing) a wide variety of materials. Laser numerically controlled micromachining satisfies these requirements. Although other techniques such as through-mask electrochemical machining is applicable to shim production, this paper will emphasize the use of laser micromachining for preparing individual laminates.

LIMITATIONS OF CURRENT FABRICATION METHODS

Current microelectronic integrated circuits (IC) are predominately silicon-based. MECS, on the other hand, require the mechanical and thermal properties provided by other materials. For example, many thermally-based applications require low thermal conductivity material to reduce heat transfer (Peterson, 1998 and Peterson, 1999). Other requirements for subcomponents could be for highly fatigue resistant material for springs or magnetic steels for generator and motor cores. Clearly, current IC fabrication techniques cannot be used for constructing the major components of energy-based meso devices. Similarly, many of the prevailing MEMS manufacturing technologies (Warrington, 1995, Kovacs, 1998, and Guckel, et al., 1991), are based on silicon, polymers, or electroplated pure metals (having high thermal conductivity). Adapting these MEMS fabrication techniques for the construction of MECS would be difficult to achieve.

A second requirement for MECS construction is the need for a "vertical" fabrication method for high-aspect-ratio features. Micro channel arrays with 20-to-1 aspect ratios are commonly needed for heat exchangers and regenerators. Other MECS designs may call for a small gap between adjacent sub-components where the gap is maintained for the entire length of the structure. Other MECS requirements call for heterogeneity in fabrication materials where electrical and magnetic sections may require a metal and non-conducting sections may need a polymer or ceramic. Furthermore, electronic chips to provide processing of information or communication may be needed in the overall design of MECS. This is a significant challenge for current microfabrication techniques. Current MEMS fabrication technology has not demonstrated the capability for producing the devices envisioned here.

Finally, MECS must be able to offer geometrical sophistication at low cost in order to compete with conventional macroscale energy conversion devices. The most notable high-aspect ratio MEMS fabrication technology is LIGA (Becker, et al., 1986 and Ehrfeld, et al., 1987). In addition to being primarily a polymer forming method, LIGA is dependent upon highly capital intensive synchrotron X-ray generation. Other lower cost variants of LIGA (Paul and Klimkiewicz, 1996, Holms, et al., 1997) are being developed to address this need, but capital investment is still high. LIGA and the lower cost derivatives all use lithographic techniques for mold making and electroplating for material deposition. Weaknesses of this approach include limited material selection, limited geometric complexity (two dimensional structures), and inconsistent pattern-transferring methods (Walsh, et al., 1996). Other net-shape microfabrication techniques have been exploited including laser-beam (Ihlemann et al., 1993), electron-beam (Brunger and Kohlmann, 1992), ion-beam (Martin et al., 1996), electrochemical (Datta and Romankiw, 1989), electrodischarge (Datta, 1993), and mechanical methods (Friedrich and Kikkeri, 1995) for material removal or deposition. However, all of these approaches are either 1.) serial in nature and, therefore, lack the capability of economical mass production, or 2.) involve single layer thin film forming and, therefore, provide limited aspect ratios. No well-established micromechanical fabrication method currently exists for addressing MECS device fabrication requirements in a low-cost, high-volume manner.

Oregon State University, Pacific Northwest National Laboratory (Richland, Washington), and Tektronix, Inc. (Wilsonville, Oregon), have been developing microlamination for high aspect ratio devices. The OSU and PNNL (Wegeng, 1994 and Wegeng et al., 1996) work has concentrated on MECS while Tektronix has developed their process to mass produce ink-jet print heads (Anderson, 1989). The fabrication methods being pursued by these three groups rely on building up a microlamination of thin shims and bonding them into a composite assembly. Similar to rapid prototyping techniques, microlamination involves three steps: 1.) laminate formation, 2.) laminate registration to form an assembly, and 3.) bonding of the assembly. Metal microlamination has the capacity to fabricate metal devices with high aspect ratios in large production volumes. This has been demonstrated by the existing production capability of Tektronix. The company has fabrication lines where thousands of metal ink jet print heads are being produced for commercial use. Further development of this method with metals, and other materials such as ceramics and polymers, will require research of laminate formation processes, bonding techniques, and the effects of non-ideal registration processes.

Table I lists the advantages and disadvantages of laser-based microlamination. The comparison is made with regard to the current state of micro and meso fabrication techniques. Although using laser micromachining for laminate formation is an inherently serial process, for research purposes, it offers distinct advantages over electrochemical machining (an inherently batch-wise process). The main advantage is the rapid progression from design to cut laminate without the need for generating a mask. For mass production of a mature device, chemical and electrochemical processes probably have cost advantages over laser micromachining. However, with the continued improvement in the power and speed of laser micromachining, especially with the advent of diode pumped YAG lasers, this advantage may not exist in the next few years.

Table I
Advantages of Microlamination with Laser Micromachining
1.) Wide selection of material properties are available to suit a particular application. Material can be metal, ceramic, or a polymer with specific and tailored properties, e.g. low thermal conductivity, high temperature materials can be used, or steels with high magnetic permeability.

2.) Versatility in pattern design and aspect ratio. Specific lamination design can be created on a computer and then generated by numerical controlled laser machining in relatively few steps. Many laminates can be stacked to provide high aspect ratios.
3.) Quick progression from design to final device — no masking is necessary. Mask production introduces additional steps into the prototyping process.
4.) Feature size limitation well suited for mesoscopic devices. Feature sizes as small as 10 µm can be generated (dependent on the material being machined). Easy to generate large features as well.
5.) Little shape warpage during assembly and bonding. Depending on the bonding method selected, little-to-no variation in the laminate shape is observed. Majority of shape variation resides in the registration step.
6.) Hybrid structures of different materials can be assembled into a single package.
7.) Full system integration into a single block of material can be achieved thus providing a simple, but powerful technique for system development.
8.) Dissociated features can be created in the final device allowing greater versatility in developing unique functional sub-components in the final product.
9.) Although laser machining is inherently serial in cutting features, all other steps in the fabrication process can be carried out in a batch-wise manner.

Table II
Disadvantages of Microlamination with Laser Micromachining
1.) Minimum feature size is currently limited to approximately 5 to 10 µm. This is dependent on the thickness of the laminate being cut and the wavelength used. Future developments will allow smaller feature sizes.
2.) Most structures cut in single laminates are inherently two-dimensional. This can lead to design limitations in the final device.
3.) Some surface preparation is typically needed after laminates are cut thus increasing the number of processing steps.
4.) Some specialized equipment is needed, e.g. a laser micromachining system and a vacuum hot press (for bonding).
5.) Bonding techniques based on diffusion soldering and brazing require an additional plating step.
6.) Laser machining can create a heat affected zone along the cut.

LASER MICROMACHING OF LAMINATES

Laser micromachining can be accomplished with pulsed or continuous laser action. Machining systems based on Nd:YAG and excimer lasers are typically pulsed while CO_2 laser systems are continuous. Much of our experience has been with the former system using an Electro Scientific Industries model 4420. This micro machining center uses two degrees of freedom by moving the focused laser flux across a part in a digitally controlled x-y motion. The laser is pulsed in the range between 1 and 3 kHz giving a continuous cut if the writing speed allows pulses to overlap. The cutting action is either ablative, or semi-ablative depending on the material being machined and the wavelength used (either the fundamental at 1064 nm, the second harmonic at 532 nm, or the third harmonic at 355 nm). The drive mechanism for the laser is a digitally controlled servo actuator giving a resolution of approximately 2 µm. The width of the through cut, however, is dependent on the focused beam diameter.

We have also had laminates machined with CO_2 laser systems. Commercial laser machining services are available for cutting metal sheet for use in a variety of applications, especially in the testing and development of electrical machinery (motors and generators). Most of the commercial CO_2 lasers semi-ablate or liquefy the material being cut. A high velocity gas jet is often used to help with debris removal. As with the Nd:YAG systems, the laser (or workpiece) is translated in the x-y directions to obtain a desired pattern in the material. Comparative advantages of each system are that CO_2 laser systems generate more power and can cut through thicker material (upwards of several millimeters), but the Nd:YAG systems provide smaller spot sizes giving much greater capability for micromachining of thin laminates. When cutting metals, both systems benefit from post cleanup of the laminate using either a chemical wash or physical polishing to remove debris. For microlamination, it is critical that no ridging or crust remain on the laminates. Laser micromachining, in the non-ablative mode, produces some of these non-desirable features on the cut surface. Thus, post clean up of the part is necessary. However, with an ablative mechanism, such as that obtained when cutting polyimide or even some metal with UV radiation, little post cleaning is needed.

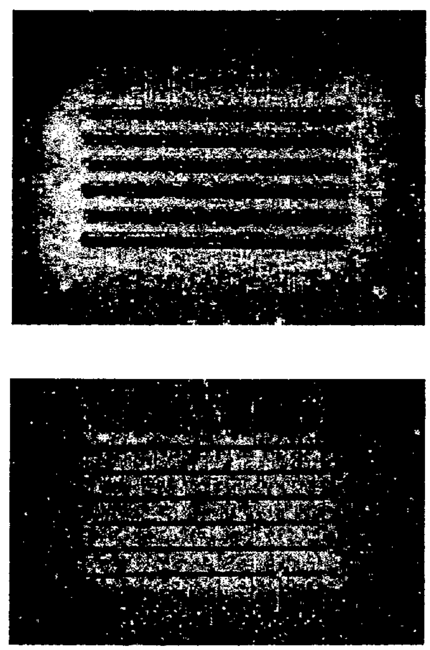

Figure 1: Laser machined lines in 90-µm-thick stainless steel. Top photo shows front side while bottom photo shows back side.

Figure 1 shows the results of using a Nd:YAG pulse laser to cut through 90-µm-thick steel shim. The front and back sides of the shim are shown in the figure. The line widths for these cuts are approximately 35 µm wide, although with steel, some tapering is observed. For the 90-µm-thick sample, three passes were made using 1 kHz pulse rate, an average laser power of 740 mW, and a distance between pulses of 2 µm. Also, the cuts were made at 355 nm. Some debris and ridging can be observed along the edge of the cut on the front side, however, this material is easily removed from the surface.

Figure 2 shows an edge structure cut at 532 nm before and after surface polishing. Average laser power and pulse rate were approximately 1 watt and 1 kHz, respectively. The material was stainless steel having a thickness of 110 μm. An example of a CO_2 laser cut shim is shown in **Fig. 3**. The part is a serpentine flexural spring used in a miniature Stirling cooler. The part has been cleaned with surface polishing to remove debris. The CO_2 through-cuts are approximately 200 μm wide and also exhibit a slight taper. The width of the CO_2 laser cut was the minimum achievable with the system used.

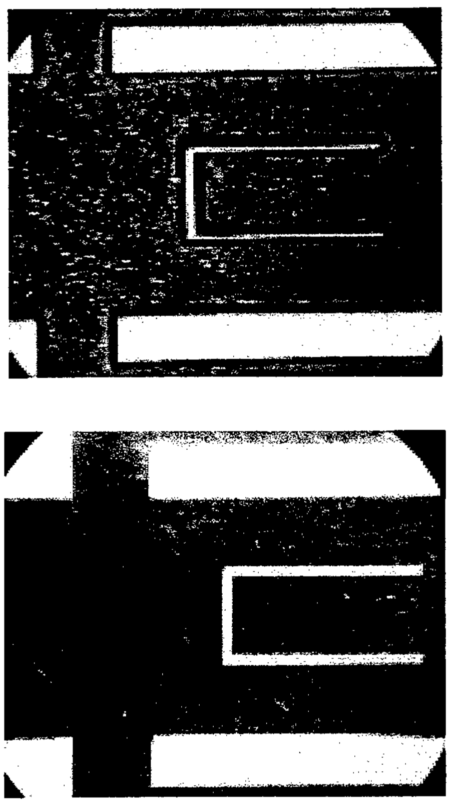

Figure 2: Laser machined laminates before (top) and after (bottom) clean-up of the part with surface polishing.

Pulsed Nd:YAG lasers have also demonstrated micromachining in polyimide material with high resolution and no debris formation. Ultraviolet wavelengths appear best for this type of work where a chemical ablation mechanism is believed to be present. Clean, sharp-edged holes in the 25 - 50 μm diameter range have been produced.

STACKING, REGISTRATION, AND BONDING

After the laminates are cut by an appropriate method, stacking, registration, and bonding of the laminates are necessary in order to produced a completed device. As an example, consider fabricating a simple, functional structure such as a micro channel array using metal microlamination. The structure is shown in **Fig. 4** where the end use could be a heat exchanger that rejects thermal energy to the environment. **Figure 4** shows the lamination scheme for prototyping the structure. In the first step, as previous discussed, the laminates are formed by micromachining metal shims. The second step is to prepare each laminate surface by cleaning and, depending on the bonding method, plating of a thin (1.0 to 10 μm) metal layer on both sides of the laminate. Next, the laminates are stacked and registered using an alignment jig. Finally, the laminates are thermally bonded at an elevated temperature while being pressed together. This entire process produces a single block of material having embedded high-aspect-ratio features. Note that if sophisticated internal structures were needed, additional steps could be included. For example, a patterned etching for surface relief could take place before metal plating to ensure specific areas on the laminates do not bond to adjacent surfaces. Also, internal structures could be released by dissociating fixture bridges (discussed later).

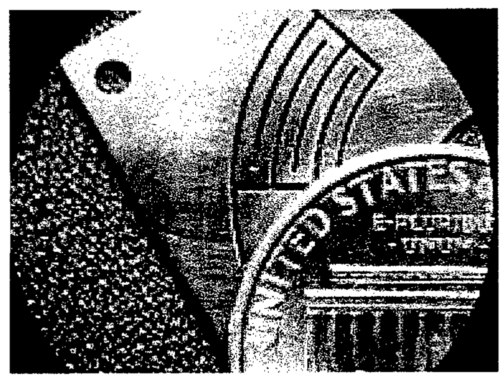

Figure 3: Serpentine spring cut with CO_2 laser machining of stainless steel (after clean up). Shim thickness is 250 μm.

Once the laminates are cut by an appropriate method, it is necessary to stack and register the laminates. The stacking order is part of the design process that yields internal structures important for device operation. In advanced designs, it may be common for a hundred or more laminates to be stacked to create a high-aspect-ratio microchannel array. But in some important devices, only a few laminates are needed. For example, a float valve requiring only five laminates is discussed in the following section. Once stacked in the proper order, each laminate must be positioned precisely in relation to its neighbors. This process is called registration and is a crucial step in the microlamination process.

The precision to which laminates can be positioned with respect to one another will often determine whether a final device will function. The complexity may range from structures such as microchannel arrays which would be somewhat tolerant of misalignment, to more sophisticated devices requiring highly precise alignment. For example, a small scale device may need a rotating sub-component requiring miniature journal bearings axially positioned to within a few microns of each other. Registration can be accomplished with an alignment jig that accepts the stack of laminates and aligns each using some embedded feature — corners and edges can work as long as they are common to all laminates. Another approach incorporates alignment features, such as holes, into each laminate at

the same time other features are being machined. Then, the alignment jig can incorporate pins that pass through the alignment holes. The edge alignment approach can register laminates to within 10 microns assuming the laminate edges are accurate to this level. With alignment pins and a highly accurate laminate machining technique, micron level positioning is feasible. One other important consideration is that the alignment jig must tolerate the bonding step. Thus, in typical microlamination setups, the alignment jig is incorporated into the design of the structure that compresses the stack for bonding.

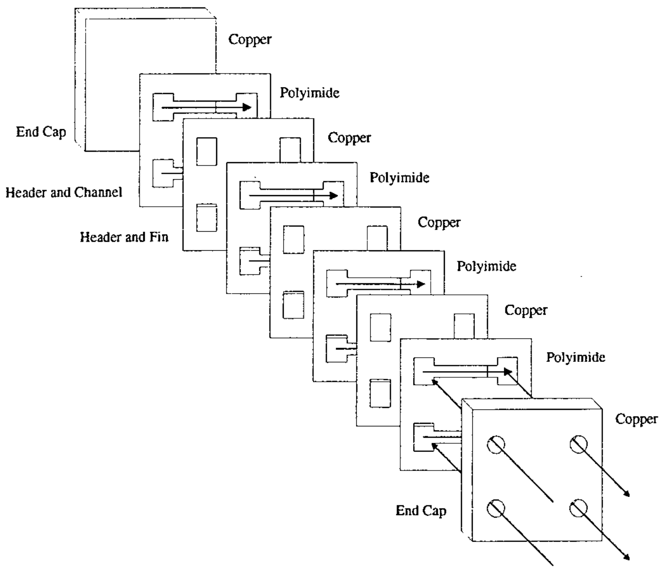

Figure 4: Microlamination sheme used to fabricate a dual micro-channel array. Arrows show direction of flow.

The laminate bonding process must form a strong, durable, and often hermetic seal between each laminate. A number of different approaches to this problem have been explored and are listed in **Table III** along with their advantages and disadvantages. One of the most promising bonding methods we are studying involves diffusion brazing and soldering.

The concept of diffusion brazing/soldering has been described previously by Jacobson and Humptson (1992). They present a number of material combinations that can be use on both base metals and on surfaces that have been metalized. Two of the more versatile combinations are tin-silver and tin-indium. These two diffusion soldering systems provide a low temperature bonding process that results in strong joints at the material interface. Another attractive feature is that the bond can take considerably higher reheat temperatures. Because of these characteristics, diffusion bonding appears ideal for producing microlaminated devices that must operate at moderate temperatures (up to approximately 500 C).

Table III
Microlamination Bonding Techniques

1.) **Polyimide Sheet Adhesive:** Polyimide is a high strength, high temperature polymer. In a special sheet formulation from Dupont called, Kapton KJ, it retains adhesive properties and can bond surfaces together when heated and compressed. This material is good for moderate strength bonds providing good sealing capability.

2.) **Diffusion Soldering and Brazing:** Requires plating of the surfaces with a low melting point metal. Tin/Silver and Tin/Indium have been used in the past for low temperature bonding. Provides a hermetic seal good up to re-heat temperatures exceeding 300 C. Best performed in vacuum hot press conditions.

3.) **Diffusion Bonding:** High strength, high temperature bonds are produced by this method. Requires high temperature, high pressure to form bond. Method can be applied to untreated (except of cleaning and oxide removal) metal surface, but techniques exist for metal plated surfaces also, e.g. stainless steel plated with gold. Often requires vacuum or reducing environments in addition to high pressures.

4.) **Micro Projection Welding:** Technique where laser machining or photolithography followed by surface etching is used to create projections on a metal surface. After laminates are stacked and bonded, electrical discharge is passed through stack heating and bonding only areas where projections make contact with adjacent parts. Can be used in air and takes place rapidly. Significant surface preparation needed.

The tin-silver system can work on any surface able to withstand moderate temperatures and capable of receiving a plating layer of the requisite metal. For many of our devices, steel and stainless steel offer a number of attractive characteristics for fatigue strength, magnetic properties, relatively low thermal conductivity (for stainless steel), and corrosion resistance. However, before the bonding can occur, the surface of each steel laminate must be prepared and plated. A typical plating process involves placing a very thin strike layer of nickel (approximately 0.5 μm) on the bare steel surface. This layer promotes adhesion of the other platable metals. Then, a copper layer 2 - 5 μm thick is plated over the nickel as a base upon which to plate either tin or silver. Copper is necessary as a bonding agent because of its ability to readily bond to both nickel and either silver or tin. Finally, a layer of tin or silver is plated 2 - 5 μm thick over the copper layer. What is desired for this last plating operation is to produce a laminate stack that will have alternating surfaces plated with either silver or tin. The two outside laminates should be silver so that the final, bonded stack does not adhere to the alignment jig. Also, our experience has shown that, if possible, non-bonded internal structures and cavities should have the silver layer on their surface. Through careful selection of which laminates to coat with tin and silver, this can usually be achieved.

The bonding takes place by momentarily raising the stack temperature above the melting point of tin (232 C) under a compression pressure of approximately 2 MPa. Careful exclusion of air (or other oxidizing atmospheres) is needed at this point to avoid the creation of tin oxides and voids. However, with the surface properly prepared, the bonding process is rapid and complete. Also, bond strength and re-heat temperatures can benefit by "cooking" the stack for a longer period of time at the bonding temperature, e.g. up to one hour. This allows tin to further diffuse into the silver and form strong intermetallic compounds within the joint itself. Some evidence exist for ultimately forming a silver bond interspersed with intermetallic tin/silver particles yielding a high strength, moderate temperature

joint. Note that indium can also be used in place of tin yielding a even lower temperature (melting point of indium is 157 C) bonding process.

SAMPLE DEVICES

In this section, a microchannel array and two types of valves are described. Each device demonstrates an important aspect of microlamination either during bonding, post-bond processing, or the incorporation of unique features into the overall design.

A.) Microchannel Arrays

As a first example of a device that can be fabricated with microlamination, **Fig. 4** shows a micro channel array. The design and stacking arrangement is shown. The device was designed to use a polymeric spacing and bonding sheet between copper micromachined shims. The bonding sheet is a polyimide material from DuPont (Kapton type KJ) that becomes active as an adhesive at temperatures exceeding 250 C. After bonding, the device has a useful service temperature under light internal pressure up to approximately 200 C. The bonding process takes place in an alignment jig using the sides and corners of the shim material as alignment features. Specific bonding conditions for the part shown in Fig. 4 was 265 C under a compression of 200 kPa. The stack is held at the bonding temperature and pressure for approximately 1 minute, then cooled. Our experience with this approach is that good, hermetic seals are formed by this method. Although clean and polished metal surfaces can be bonded together, type KJ polyimide bonds best to oxidized surfaces. Another attractive feature of this material is that under typical bonding temperatures and pressures, little flow is observed in the channel area. To date, all bonds have been accomplish in a small laboratory press surrounded by atmospheric air. We will be testing the bonding process in a vacuum press in future experiments.

The copper and polyimide laminates were cut from 100 μm-thick stock using the ESI model 4420 laser micromachining center. The output from the laser was 532 nm light from intercavity frequency doubling of the Nd:YAG fundamental. Qualitative observations were that the copper material cuts rapidly and with little debris generation on the surface. Each copper laminate was cut in approximately 45 seconds using a three pass process. This is in contrast to steel witch requires two to three times as long to cut the same thickness of material. The copper surface was physically polished to remove any debris and ridging that may have formed during the machining process. Polyimide cuts rapidly in two passes with no observable debris formation.

The final device produced after bonding was a microschannel array having 4 channels with a channel height of 100 μm, a width of 3 mm, and flow channel length of 10 mm. Headers were incorporated into the design at both ends, and as shown in the figure, top and bottom caps were used to interface the flow from a test loop to the device. Preliminary test data is shown in Fig. 5 where volumetric flow of water is plotted versus pressure head for four nominally identical devices. The theoretical curve is for laminar flow through the channels. Since the experimental curves show a slightly reduced flow rate, some influence from header design and other non-ideal flow characteristics are probably present. However, the data does suggests that laminar flow through the channel array provides a close approximation to the pressure drop.

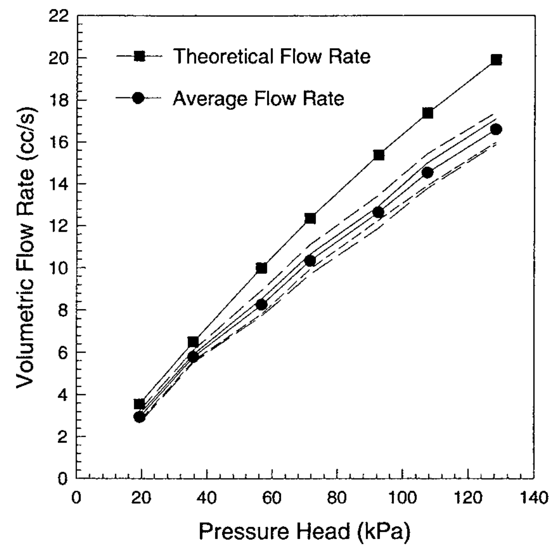

Figure 5: Flow rate vs. pressure head for four microchannel arrays. Theoretical and averaged curves also shown.

B.) Float and Flapper Valves

Two types of valves have been constructed using microlamination techniques. The major design differences between the two are shown in **Figs. 6 and 7**. The first valve was designed as a one-way float valve. It was constructed with five laminates. The design utilized an upper and lower orifice plate (laminates 1 and 5) where fluid enters and leaves the valve. The dimensions of the upper orifice was 1.5 mm in diameter while the bottom ring orifice has an outer diameter of 3 mm. In this design, the center float must be dissociated from its laminate after assembly in order for the valve to function. The second valve design was a traditional flapper assembly constructed out of two laminates. A top laminate containing the flapper was bonded to a lower orifice plate. Size of the orifice was also 1.5 mm in diameter.

The float valve design was based on a freely floating disk inside a cavity formed by two spacers, as shown in **Fig. 6**. This design calls for a special post assembly process called component dissociation which removes fixture bridging holding the float disk in place during assembly. The laminates were laser machined (532 nm output from a Nd:YAG pulsed laser) from 250 μm thick mild steel shim stock. The bonding process used in this particular design employed microprojection welding. On the back side of each laminate, a microprojection was create using acid etching through a photoresist mask. The projection formed a narrow ring around each valve component with a height of approximately 100 μm. During bonding, the laminate stack was compressed while an electric discharge was sent through the assembly. This heated and collapsed the microprojections essentially forming a weld along the length of the projections. This bonding process was accomplished in air, although future work will investigate inert gas and vacuum conditions. Also, polyimide adhesive and diffusion soldering are being studied as

possible valve bonding processes.

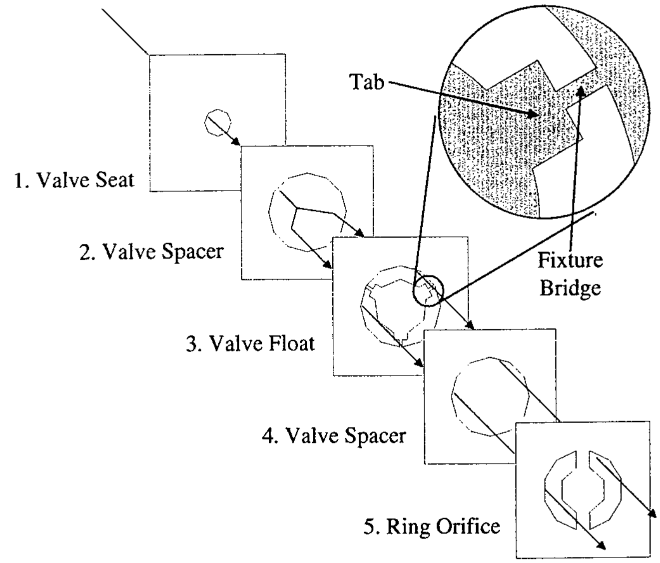

Figure 6: Lamination design for the float valve.

After bonding, the float plate is held in place with fixture bridging. Removal of this bridging can be accomplished by using a capacitive discharge process to blow the fixturing, similar to the process that a fuse undergoes when higher than rated currents flow through it. Sufficient current must be supplied to an electrode contacting the float plate (passing through the top center orifice) to vaporize the fixture bridging in one brief pulse. For the float valve results shown in **Table IV**, a 0.07 Farad capacitor bank was charged to 11 volts. With an electrode in contact with the float disk, and the body of the valve grounded, the capacitor bank was switched to connect the bank voltage to the electrode. This resulted in blowing the fixtures and freeing the float plate inside the valve cavity

Preliminary work has also been accomplished on a simple flapper valve. As shown in **Fig. 7**, a 250 μm-thick flapper plate was bonded to a 250 μm-thick orifice plate to provide the valve action. As fluid passes into the value through the bottom orifice, the flapper lifts off the orifice and provides relatively unrestricted flow through the valve. Upon flow reversal, the flapper valve seats onto the bottom plate and creates a relatively high flow resistance. The orifice diameter used in the valve was 1.5 mm. Also, the flapper was essentially a disk having a 2.2 mm outer diameter inside a larger opening having a diameter of 3 mm. To test the effectiveness of a different valve configurations, a total of 3 valves where fabricated — two having polyimide used as a seating material and one with steel-on-steel seating. Laminate material for the flapper valve was mild steel. The bonding process used for assembling the flapper valve was microprojection welding.

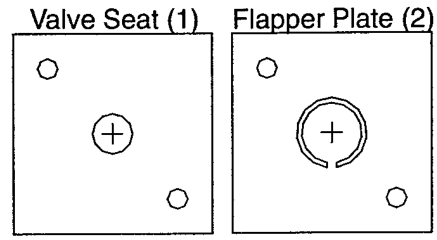

Figure 7: Flapper valve laminates showing pivoting flapper and orifice plate.

The valves were tested to asses their "diodicity", that is, their ability to restrict flow in one direction while allowing it in the other. This valve property is determined by measuring the forward and reverse mass flow rates under the same magnitude of pressure drop in the forward and reverse directions. The tests were conducted using ΔP's ranging from zero to 10.6 kPa. **Table IV** shows the performance of the flapper valve for three different valve seating configurations. The diodicity achieves values as high 6.32 for valves with polyimide on the sealing side of the flapper. Values are also given in the table for polyimide place on the valve seat, although the diodicity was not improved with this configuration. A full assessment of valve performance has not yet been accomplished and some non-ideal component effects may be present such as warpage (**Fig. 8**), incomplete laminate contact after microprojection welding, and mis registration. These factors, as well as others, will need to be examined in detail before a final assessment can be done. Improvement in valve sealing, and hence diodicity, is expected once the laminate cutting, registration, and bonding steps are refined.

Table IV

Diodicity Results for Flapper and Float Valves

	Average	Maximum
Flapper Valve:		
(with Polyimide on Back of Valve)	4.08	6.32
(with Polyimide on Valve Seat)	1.22	1.78
(No Polyimide)	1.71	2.90
Float Valve:		
(No Polyimide)	11.19	17.10

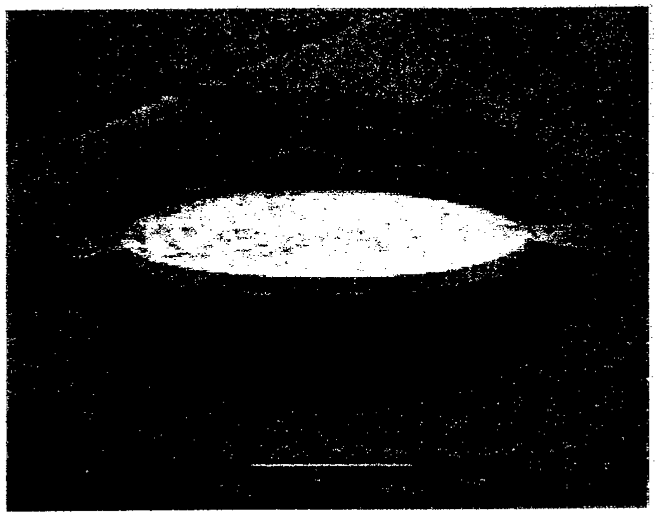

Figure 8: Microfloat valve showing warpage due to volumetric expansion caused by microprojection welding.

CONCLUSION

The work presented here demonstrates the utility of microlamination for fabricating microtechnology-based energy and chemical systems. With the capability offered by laser micromachining, miniature devices can be rapidly moved from concept to testing on the benchtop in relatively few steps. Critical subcomponents can have feature sizes down to approximately 10 μm, although most features are currently in the 50 - 100 μm size range. Many choices exist for the bonding step required to form a device from a registered stacked of laminates. The two methods studied most so far are polyimide sheet adhesive and diffusion soldering. Both produce acceptable bonding and sealing of prototype devices. However, further work on the registration and bonding steps is needed in order to move the microlamination method into a routine fabrication technique for MECS devices.

REFERENCES

Anderson, J.J., 1989, U.S. Patent 4,875,619, Brazing of Ink Jet Print Head Components Using Thin Layers of Braze Material.

Becker, E.W., W. Ehrfeld, P. Hagmann, A. Maner, and D. Munchmeyer, 1986, "Fabrication of microstructures with high aspect ratios and great structural heights by synchrotron radiation, galvanoforming, and plastic molding (LIGA process)," *Microelectronic Engineering*, Vol. 4(1): pp. 35-56.

Benson, R. S. and J.W. Ponton, (1993), "Process Miniaturization- A Route To Total Environmental Acceptability?" *Trans. IChemE*, Vol. 71, Part A, pp.160-168.

Brunger, W.H. and K.T. Kohlmann, (1992), "E-beam induced fabrication of microstructures," *Proc. IEEE Micro Electro Mechanical Systems*, Travemunde, Germany, February 4-7, pp. 168-170.

Datta, M. and L.T. Romankiw, (1989), "Application of chemical and electrochemical micromachining in the electronics industry," *J. Electrochemical Society*, Vol. 136(6): pp. 285C-292C.

Datta, M., (1993), "Anodic dissolution of metals at high rates," *IBM J. Res. Dev.*, Vol. 37(2): pp. 207-226.

Ehrfeld, W., P. Bley, F. Gotz, P. Hagmann, A. Maner, J. Mohr, H.O. Moser, D. Munchmeyer, W. Schelb, D. Schmidt and E.W. Becker, 1987, "Fabrication of microstructures using the LIGA process," *Proc. IEEE Micro Robots and Teleoperators Workshop*, p. 160.

Friedrich, C. and B. Kikkeri, (1995) "Rapid fabrication of molds by mechanical micromilling: process development," *Proc. SPIE*, 2640: pp. 161-171.

Guckel, H., K.J. Skrobis, T.R. Christenson, J. Klein, S. Han, B. Choi and E.G. Lovell, 1991, "Fabrication of assembled micromechanical components via deep X-ray lithography," *Proc. IEEE Micro Electro Mechanical Systems*, pp. 74-79.

Haas, R.W., (1995), "Further Development of MMW and SMMW Platelet Feed Horn Arrays," *Asron. Soc. Pac. Conf. Ser.*, Vol. 75, pp. 99-105.

Haas, R.W., D. Brest, H. Mueggenburg, L. Lang, and D. Heimlich, (1993), Fabrication and Performance of MMW and SMMW Platelet Horn Arrays," Intl. J. Infrared and Millimeter Waves, Vol. 14(11), pp. 2289-2293.

Holmes, A.S., S.M. Saidam and R.A. Lawes, (1997), "Low cost LIGA processes," *IEE Microengineering Technologies and How to Exploit Them*, IEE, London, UK: p. 54.

Ihlemann, J., H. Schmidt, and B. Wolff-Rottke, (1993), "Excimer laser micromachining," *Adv. Materials for Opt. Electr.*, Vol. 2: pp. 87-92.

Jacobson, D.M. and G. Humpston, (1992), "Diffusion Soldering," *Soldering and Surface Mount Technology*, No. 10, February, pp. 27-32.

Koeneman, P. B., I. J. Busch-Vishniac, and K. L. Wood, (1997), "Feasibility of Micro Power Supplies for MEMS," *J. MicroElectoMechanical Sys.*, Vol. 6(4), pp. 355-362.

Kovacs, G.T.A., 1998, "Micromachined Transducers: Sourcebook," McGraw-Hill Company, New York, pp. 19-154.

Little, W. A., (1990), "Microminiature Refrigerators for Joule-Thomson Cooling of Electronic Chips and Devices, " *Advances in Cryogenic Engineering*, Vol. 35, pp. 1325-1333.

Martin, P.M., W.D. Bennett and J.W. Johnson, (1996) "Microchannel heat exchangers for advanced climate control," *Proc. SPIE*, 2639: 82-8.

Paul, B.K. and M. Klimkiewicz, (1996), "Application of an environmental scanning electron microscope to micromechanical fabrication," *Scanning*, Vol. 18(7): pp. 490-496.

Peterson, R.B., 1999, "Numerical Modeling of Conduction Effects in Microscale Counterflow Heat Exchangers," *Microscale Thermophysical Engineering*, Vol.3, pp. 17-30.

Peterson, R.B., 1998, "Size Limits for Regenerative Heat Engines," *Microscale Thermophysical Engineering*, Vol. 2, pp. 121-131.

Warrington, R.O., 1995, "An overview of the miniaturization technologies," *Proc. SPIE - Intl. Soc. Opt. Engr.*, 2640, pp. 10-15.

Walsh, S.T., R. Boylan, R. Warrington, and J. Elders, (1996), "The emerging infrastructure for MEMS based sensor innovation," *Proc. Sensors Expo*, Anaheim, p. 431.

Wegeng, R.S. and M. K. Drost, (1994), "Developing Miniature Energy Systems," *Mechanical Engineering*, ASME, New York, NY, September.

Wegeng, R.S., C.J. Call, and M.K. Drost, (1996), "Chemical system miniaturization," *Proceedings of the AIChE Spring National Meeting*, February.

Young, M., (1997), "Platelet-Cooled Plasma Arc Torch," DOE Contract No. DE-AR21-93MC30361, Technology Development Data Sheet, (Morgantown, WV: Federal Energy Technology Center, 1997), pp. 5-6.

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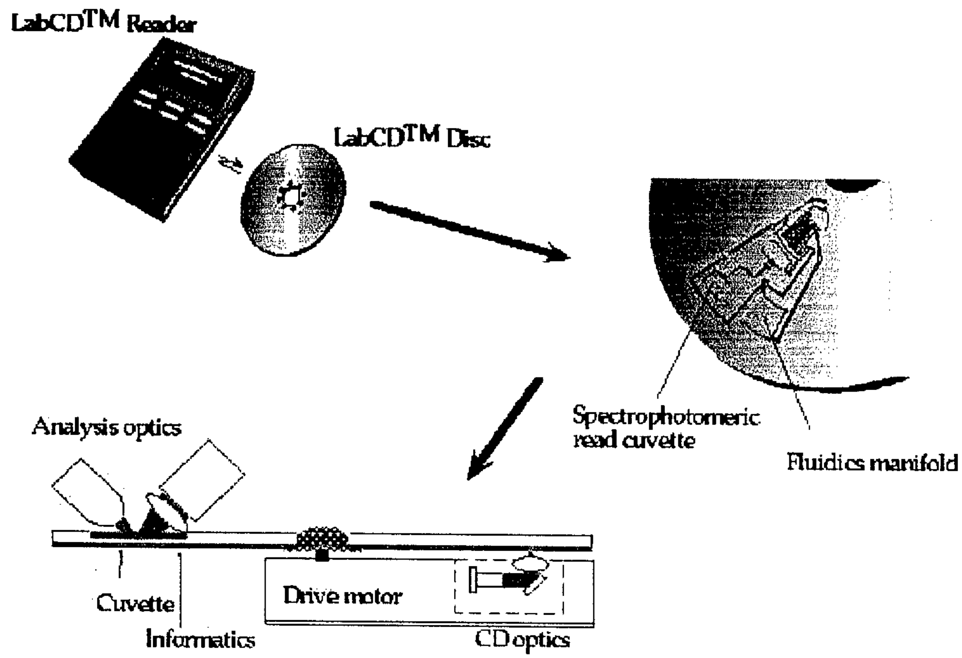


The LabCD platform consists of a plastic disc in which fluid propulsion is primarily controlled by the application of centrifugal force through a motor at the hub of the microfluidic disk. By using various rotational speeds and a combination of "passive" (pressure-dependent) or "active" (pressure-independent) valves, a wide range of fluidic processes may be carried out. The CD laser optics is used both to read and store information and modified CD optics are used in the analysis. The rotation of the analytic structure and the inertia of the fluid contained in it provide the pumping force [GAMERA Bioscience]

OUTLINE

Micro-machining (master fabrication)

- CNC-Machining and Laser Ablation
- Photolithography and Electroplating

Micro-molding (replication)

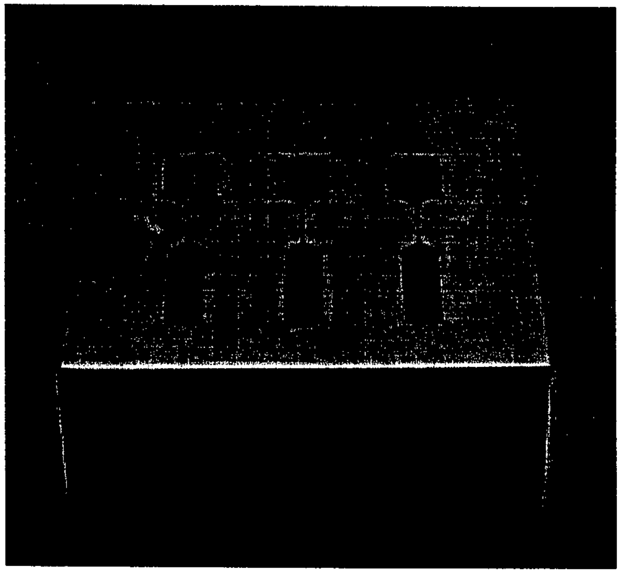
- Reaction Injection Molding/Transfer Molding
- Hot Embossing
- Injection Molding (Injection Compression and Thin Wall)

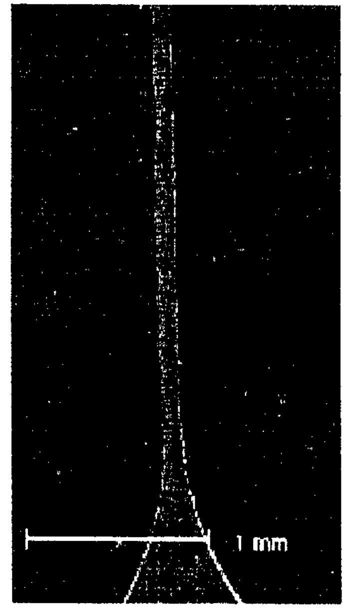
Bonding

- Thermoset Adhesive
- Organic Solvent Adhesive
- Plastic Welding

Fluid Flow in Microfluidic Devices

CNC Machining of Master





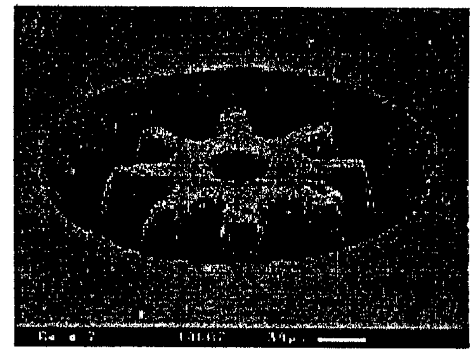
Advantage:
- Tool steel and stainless steel can be machined easily.
- Good for larger structures (>50 µm) and 3D features.

Disadvantage:
- Tolerances and repeatability in the range of 2.5~7.5 µm, so not suitable for small features.
- Not good for sharp corners or right angles.
- Surface quality is difficult to control.

Laser Microablation for Metal Masters

- Laser-milled metal features
  - ~ 10 micron width
  - ~ 10/1 aspect ratio
- Challenges
  - taper, surface finish
- Femtosecond pulse lasers
  - thin recast layer, excellent resolution

30 μm



- Femtosecond laser-machined shape in 1mm-thick copper

C. Momma, et.al. App Sur Sci 109/110:15-19, 1997

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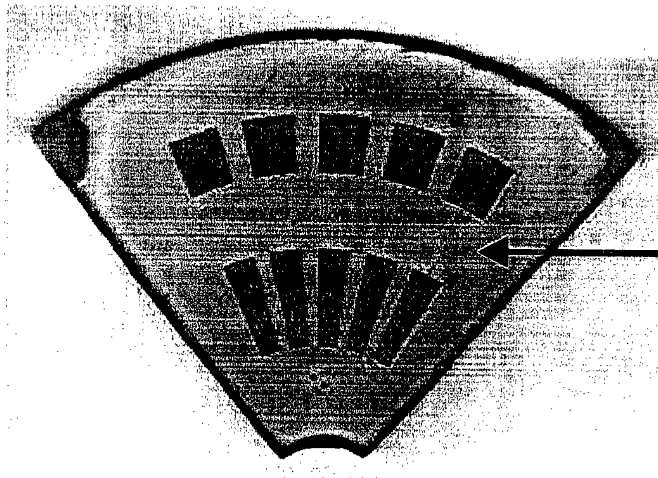
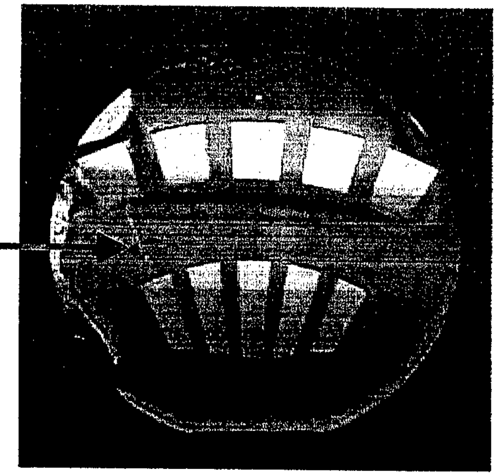
Micro-flow Device Made by Photolithography



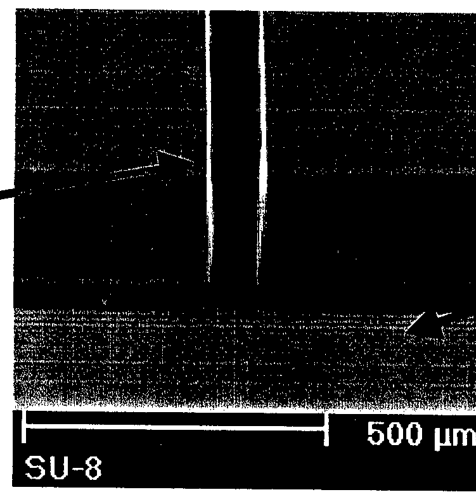
Channel width
150~5 μm



Surface micro-machining
on a CD plate

Surface micro-machining
on a silicone wafer

Channel



Chamber

Polymer Molding (Replication) Techniques

Reaction Injection Molding (RIM) / Transfer Molding (TM)

Optical Clear Reactive Liquid Resins, e.g. [illegible], *urethanes,*
silicone rubbers, crosslinkable acrylics, hydrogels

A — Ease of mold filling and low stress on master (low viscosity)
High chemical and thermal resistance (crosslinking)
Good for small, high aspect ratio, and 3D features (low viscosity)

D — Long cycle time and polymerization shrinkage (reactive processing)
Contamination (resin residue)

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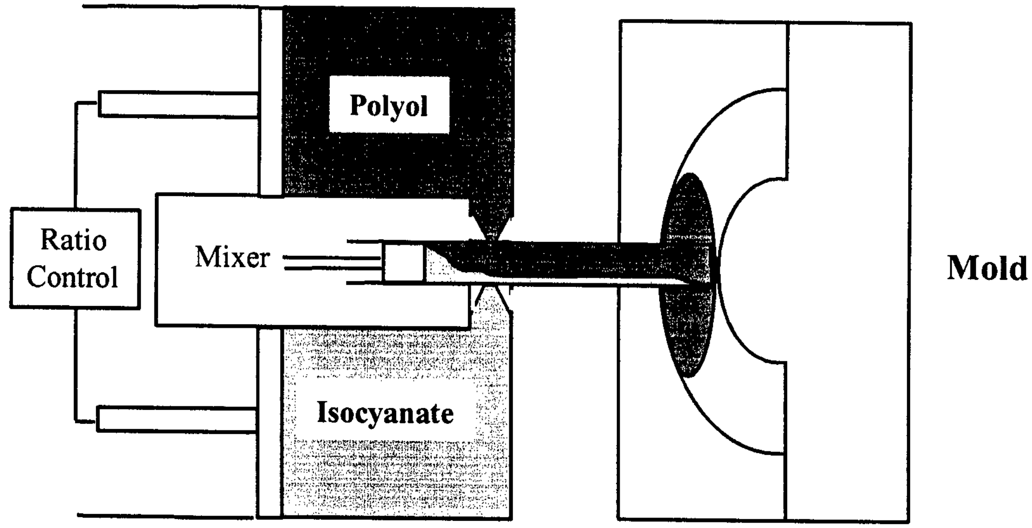
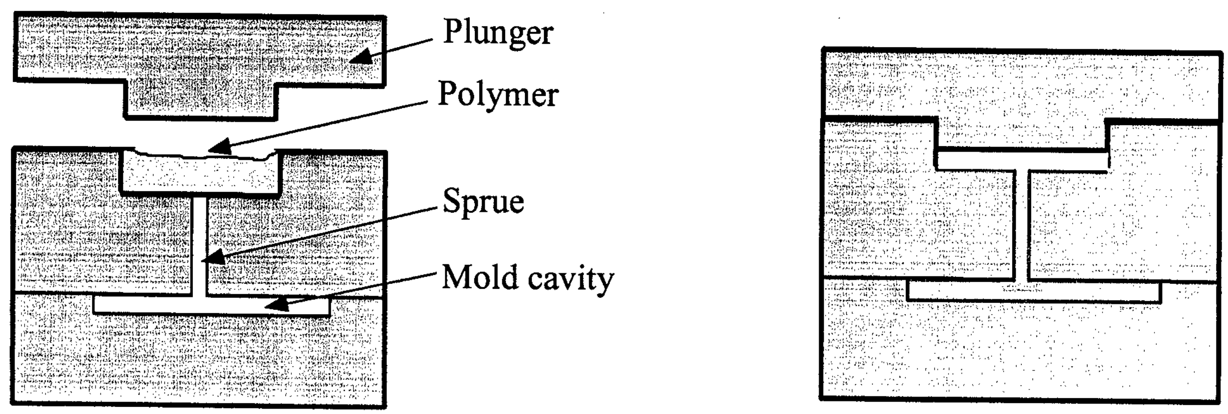
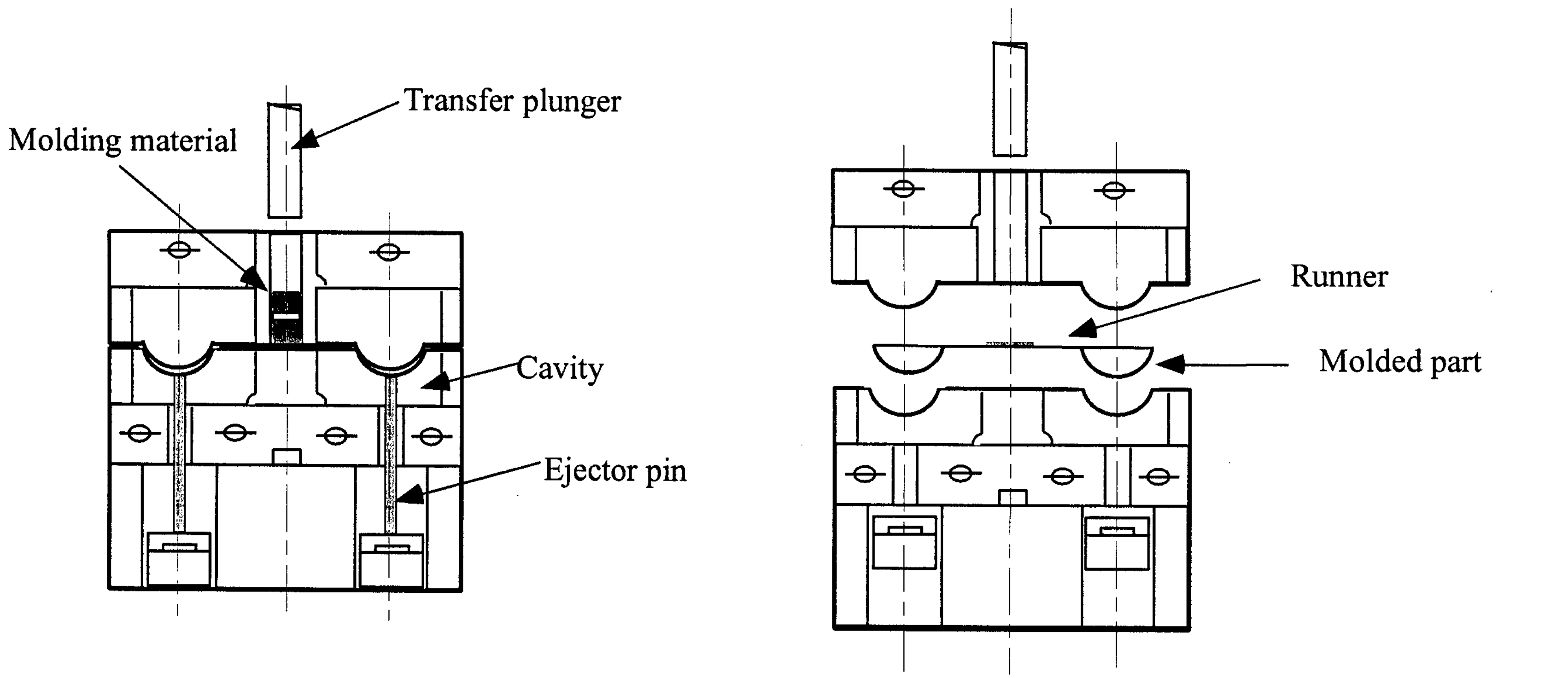
Reaction Injection Molding (RIM)



Transfer Molding (TM)



Multi - Cavity Transfer Molding



POLYMER MOLDING (REPLICATION) TECHNIQUES

Hot Embossing

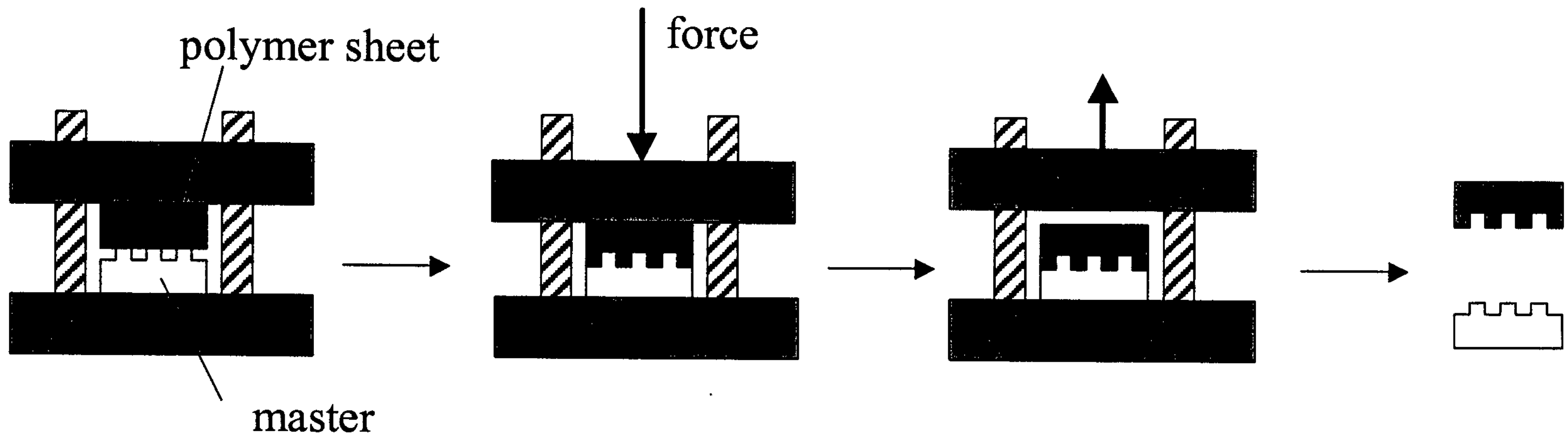
Optical Clear Thermoplastic Sheets, e.g.
Polymethylmethacrylate (PMMA)

A — Low polymer flow
Simple process
Continuous or cyclic
High molecular weight polymers

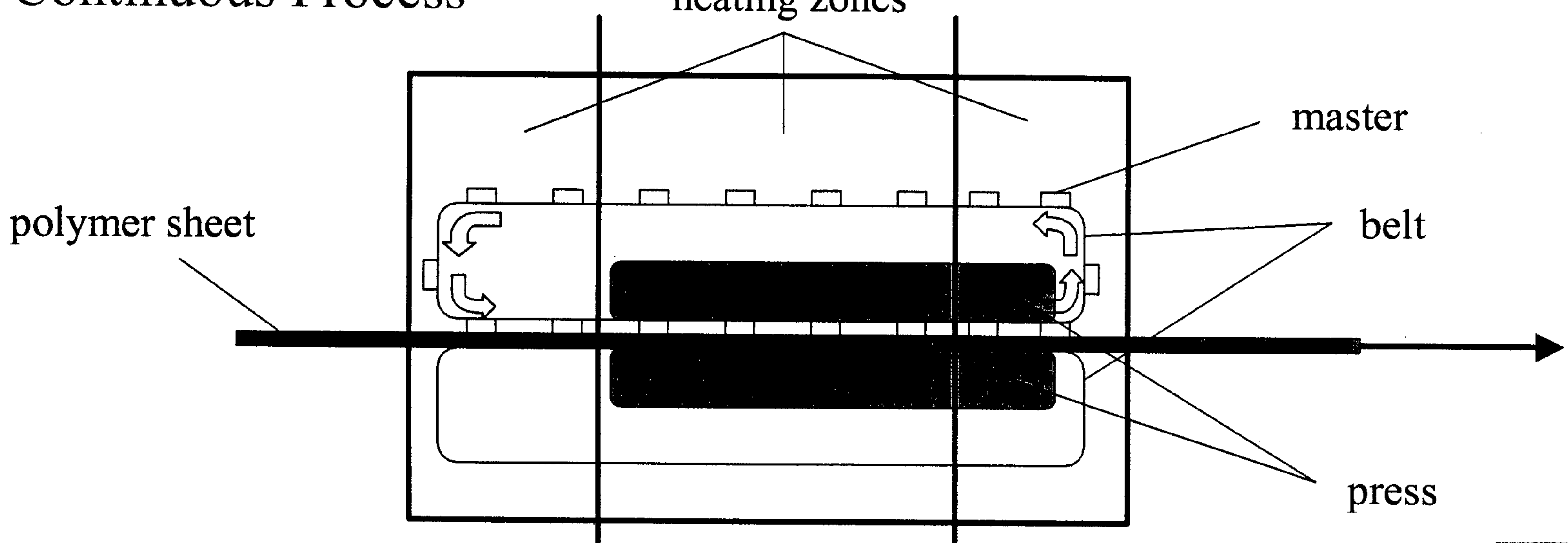
D — More difficult for structures with high aspect ratio (near T_g processing)
Less dimension control (open mold process)
Planar features only
High residual stresses on molded parts

HOT EMBOSSING

Cyclic Process



Continuous Process



Polymer Molding (Replication) Techniques

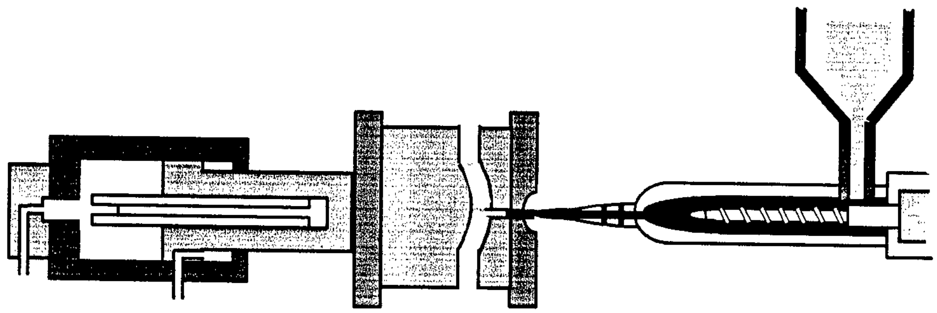
Injection Compression Molding and Thin Wall Injection Molding

Optical Clear Thermoplastic Pellets, e.g. Polymethylmethacrylate (PMMA)

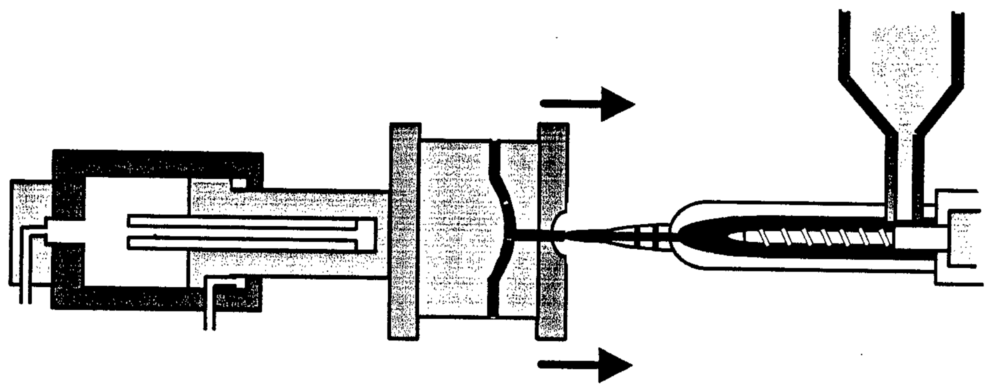
A — Good for large, high aspect ratio and 3D features
Excellent dimension control
Short cycle time

D — More expensive equipment
Cyclic process only
High stress on master
High residual stresses on molded parts
Low molecular weight polymers

Typical Injection/Compression Molding Cycle Sequence



Injection



Compression

Basic Thin Wall Injection Molding Process Description

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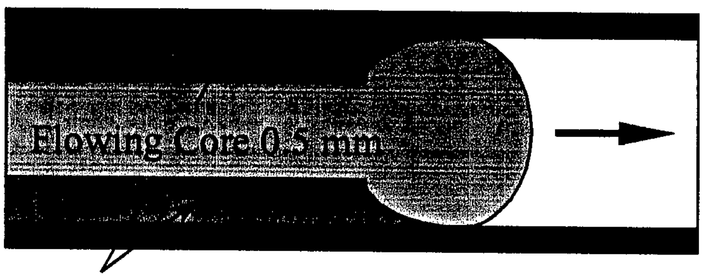
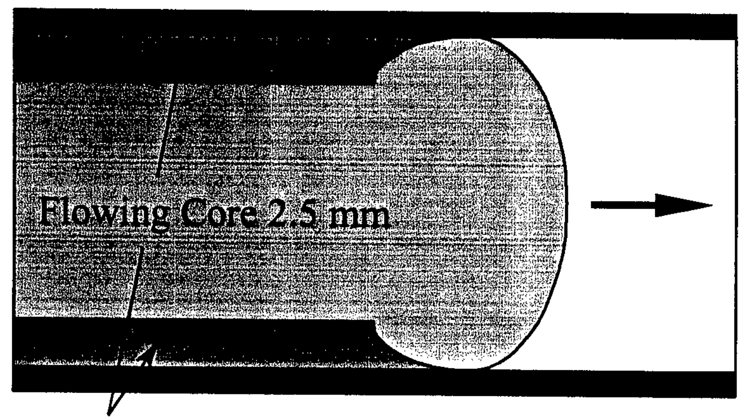
Thin-Wall Part
(1 mm)

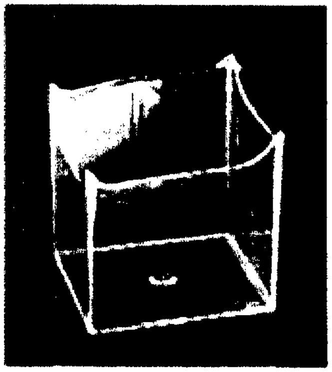


Solid Skin 0.25 mm

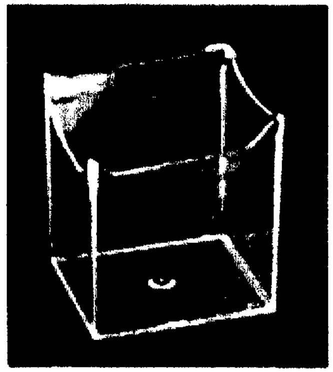
Conventional Part
(3 mm)



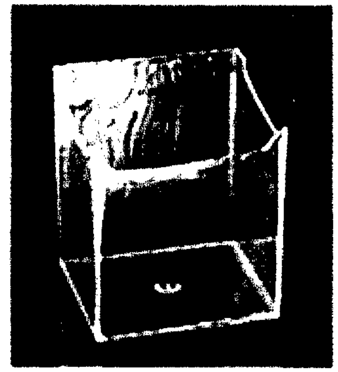
Solid Skin 0.25 mm



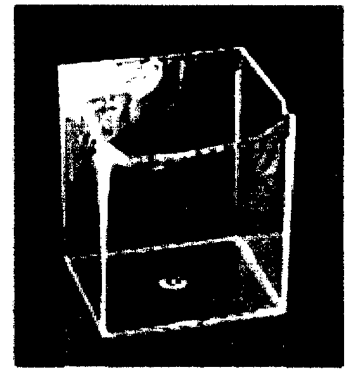
400mm/sec



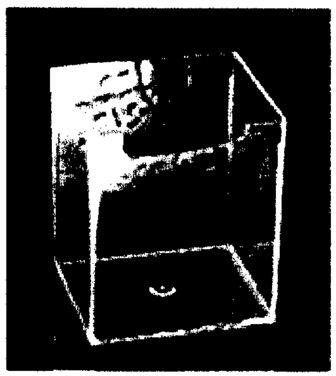
500mm/sec



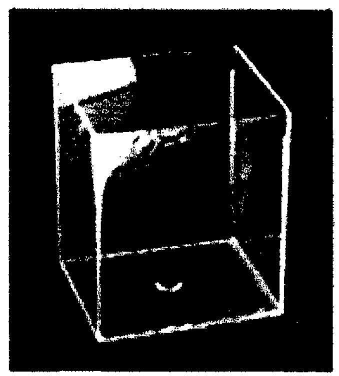
600mm/sec



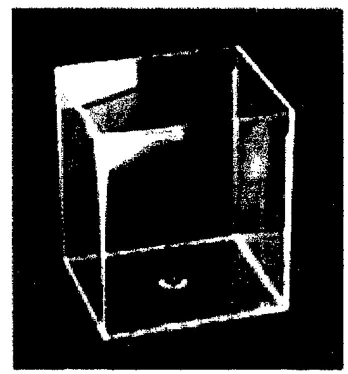
700mm/sec



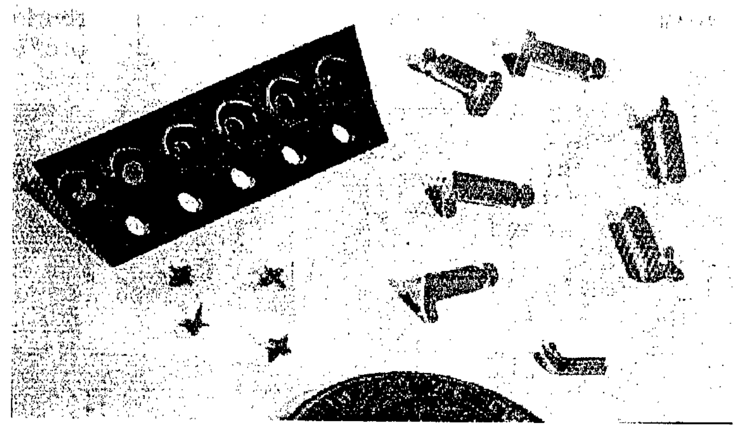
800mm/sec



900mm/sec

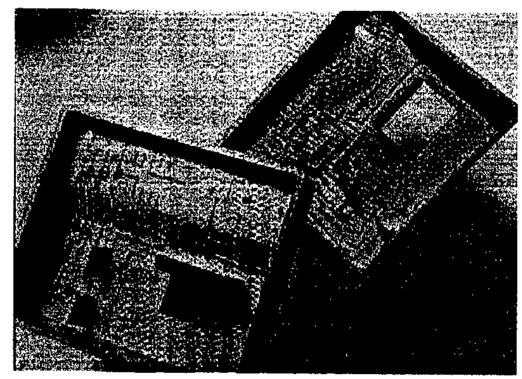


1000mm/sec



Tiny polyamide watch gears are packaged in a plastic strip (left),
Angled polycarbonate sensors are implanted in human ears to help improve hearing. [Battenfeld]

High-precision gears, pulley, and helixes are a growing market. [Axxicon]



Interconnect flash switch is made using two-component molding. [Engel]

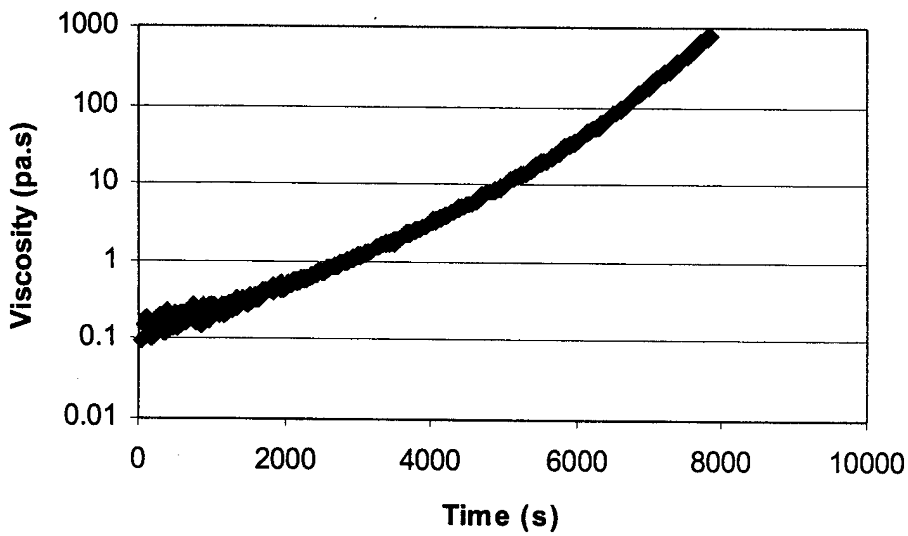
Micro-Molding

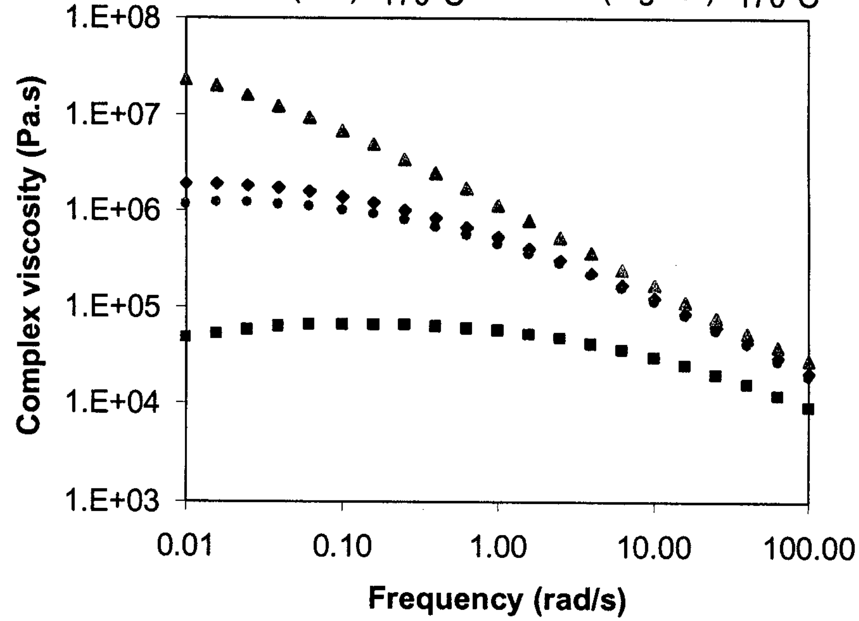
Reactive Casting
- Epoxy resin (LECO)
- Room temperature cure

Hot Embossing (30 ton Wabsh Press)
- Regular PC (GE Plastics, Lexan, Tg=145°C), OQ PC (GE Plastics, Lexan Tg=135°C)
- Compression force: 5~25 ton
- Compression temperature: 150 and 170°C
- Demold temperature: room temperature, 130°C, 150°C
- Thermal cycle: 0~115°C

Thin Wall Injection Molding
(Sumitomo 200 ton High Pressure, High Speed Machine)
- OQ PC (GE plastics, Tg=135°C)
- Melt temperature: 290°C
- Mold temperature: 30°C
- Injection speed: 0.5, 1, 2, 4 inch/sec

Resin Rheology





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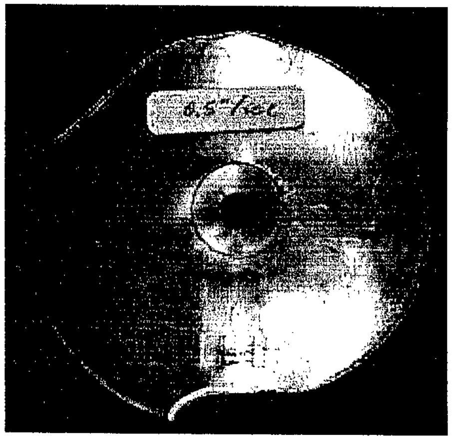
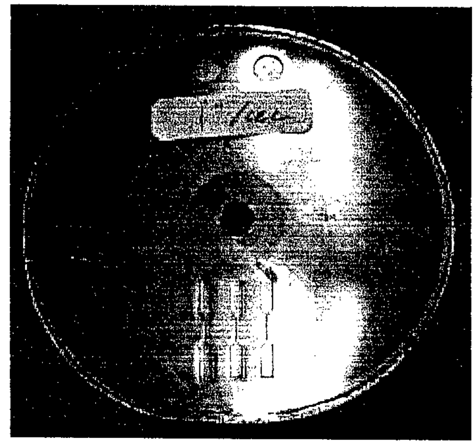
Devices Made at Different Injection Rates

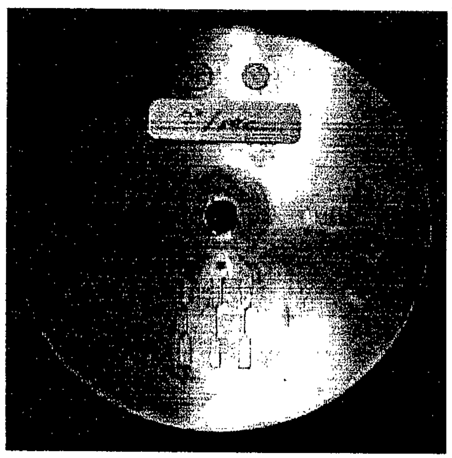
0.5"/sec



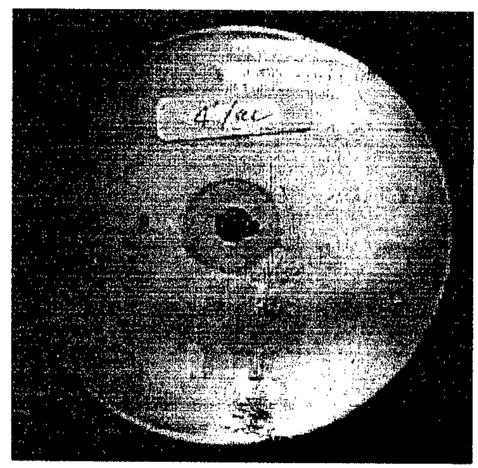
1"/sec



2"/sec



4"/sec



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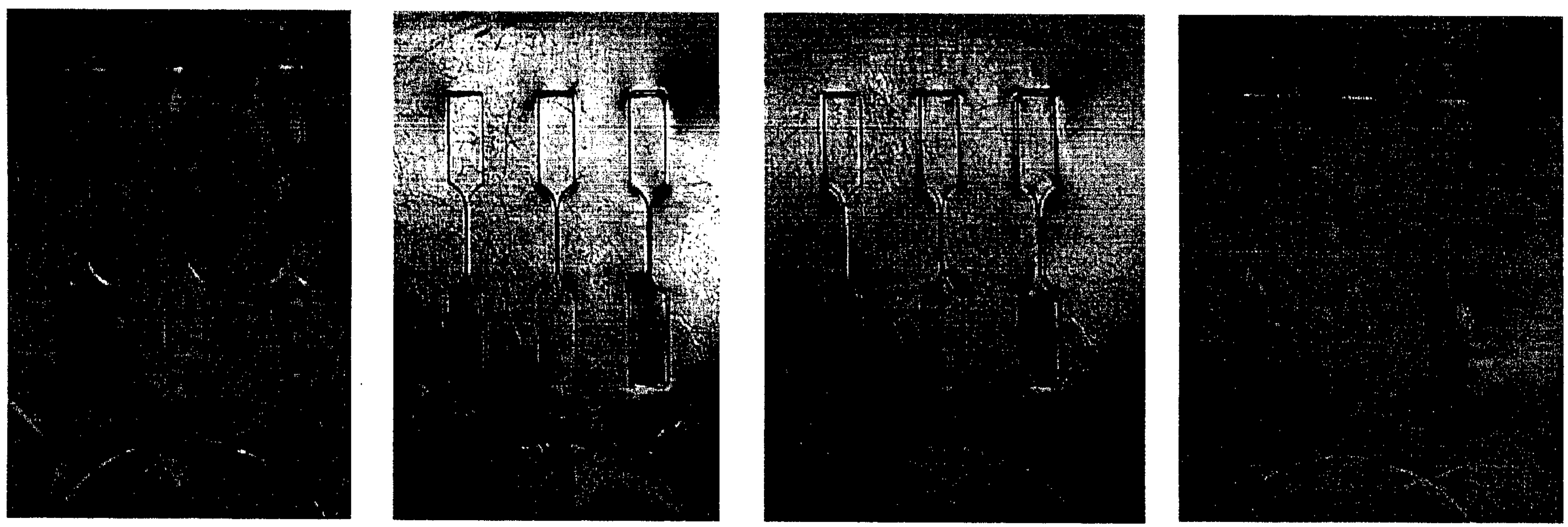
Birefringence of Devices Made at Different Injection Rates

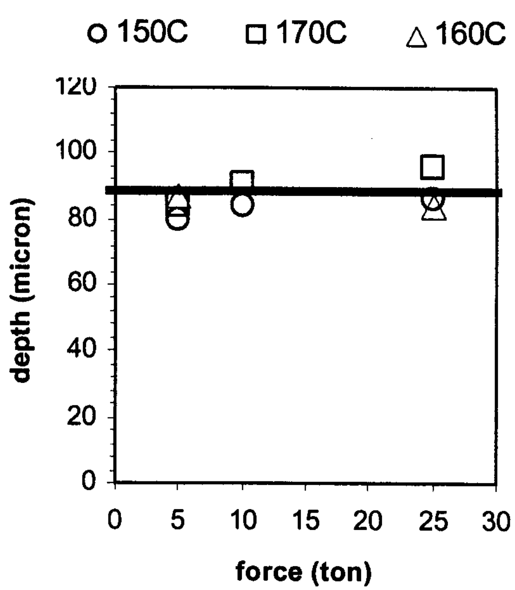
0.5”/sec | 1”/sec | 2”/sec | 4”/sec



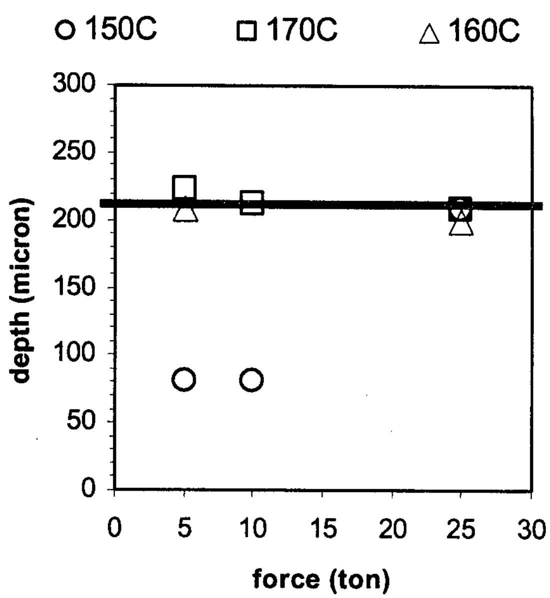
Embossing on Regular PC (Tg=145°C)

Mold temperature: 150°C (Tg+5°C), 160°C (Tg+15°C) and 170°C (Tg+25°C)
Compression time: 5 min at mold temperature, and 2-hr cooling

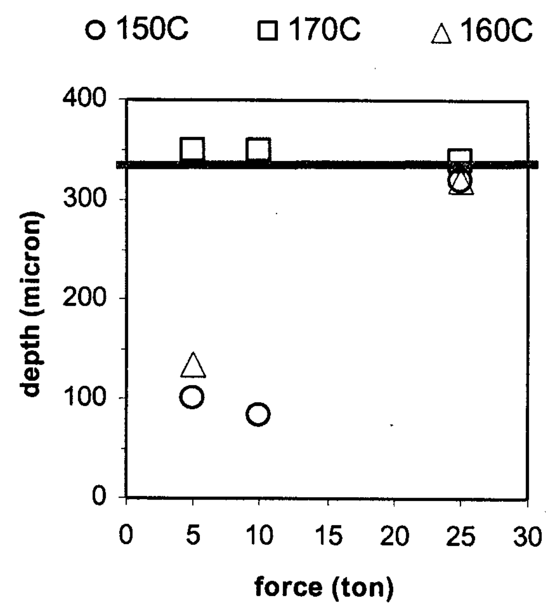
Small channel
(depth/width=92/57μm)



Medium channel
(depth/width=220/120μm)



Large channel
(depth/width=340/170μm)



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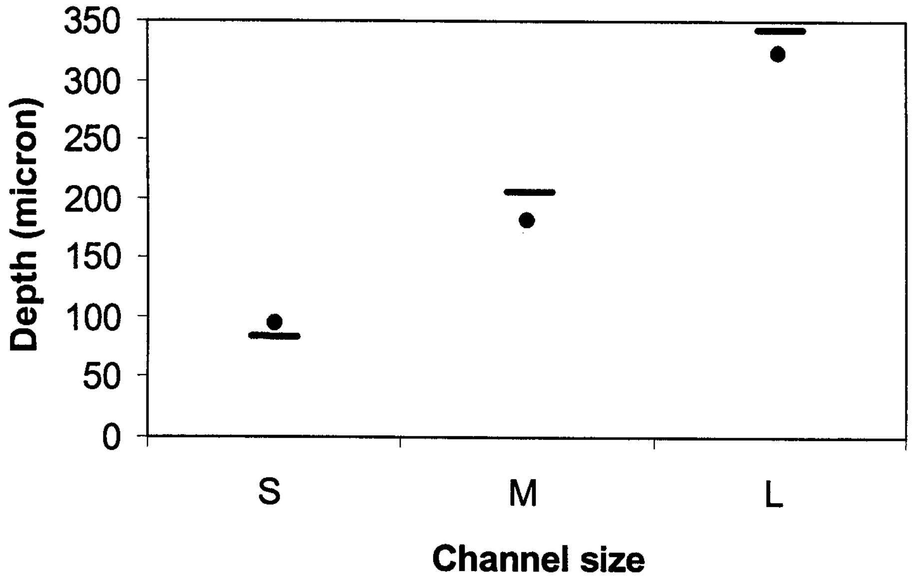
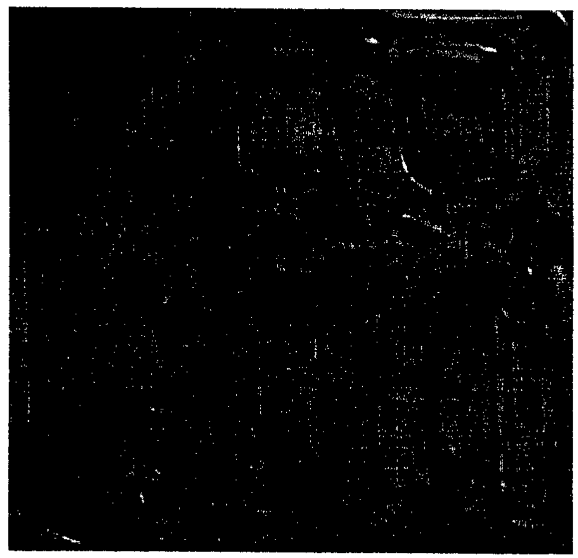
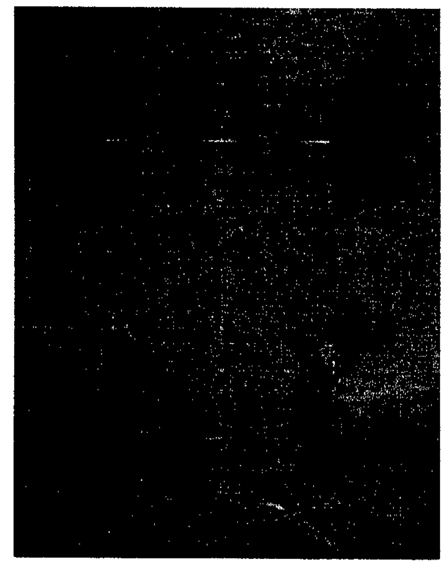
Embossing on OQ PC (Tg=135°C)

- Demold at 130C [16 min from 150C(Tg+15C) to 130C(Tg-5C)]



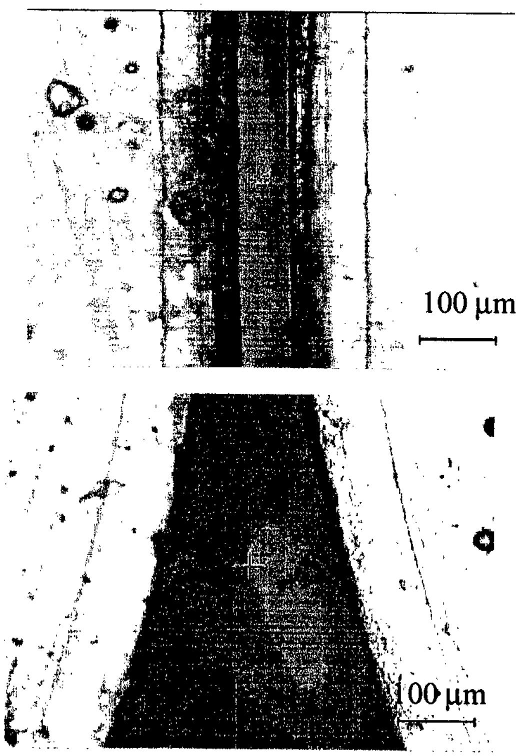
Force: 25 ton
Mold temperature: 150°C
Thermal cycle: 20°C
Compression time: 10 sec followed by 16-min cooling

Birefringence

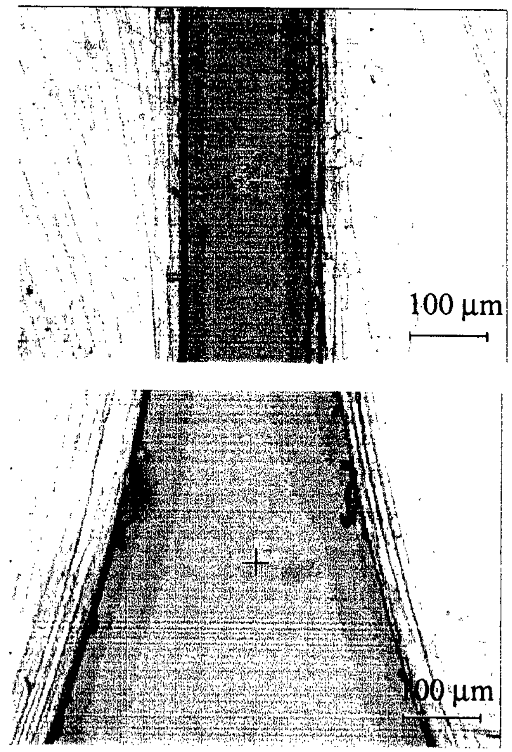
Reactive Casting (Epoxy resin)	Hot Embossing (OQ PC)	Injection Molding (OQ PC)
		

Channels under Optical Microscope

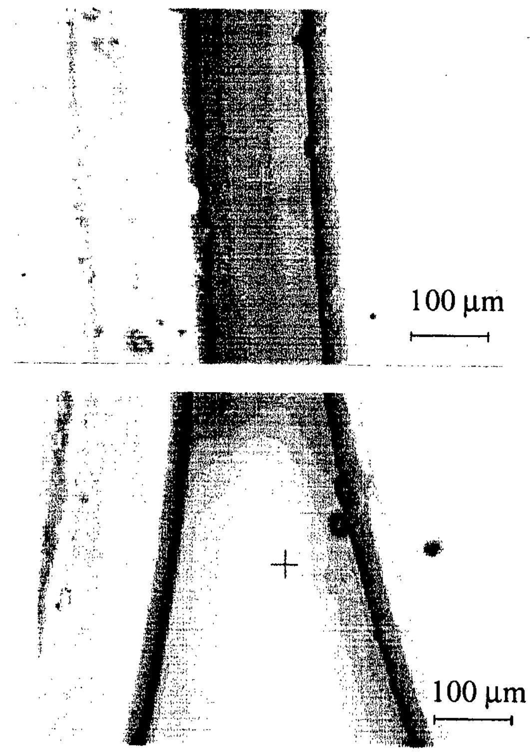
Reactive Casting



Hot Embossing



Injection Molding



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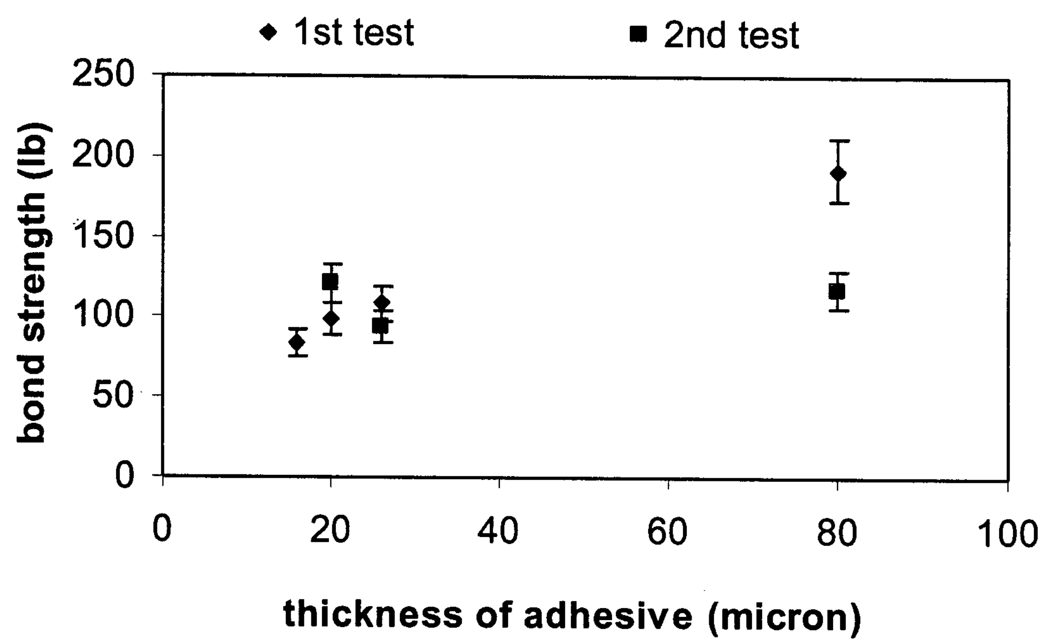
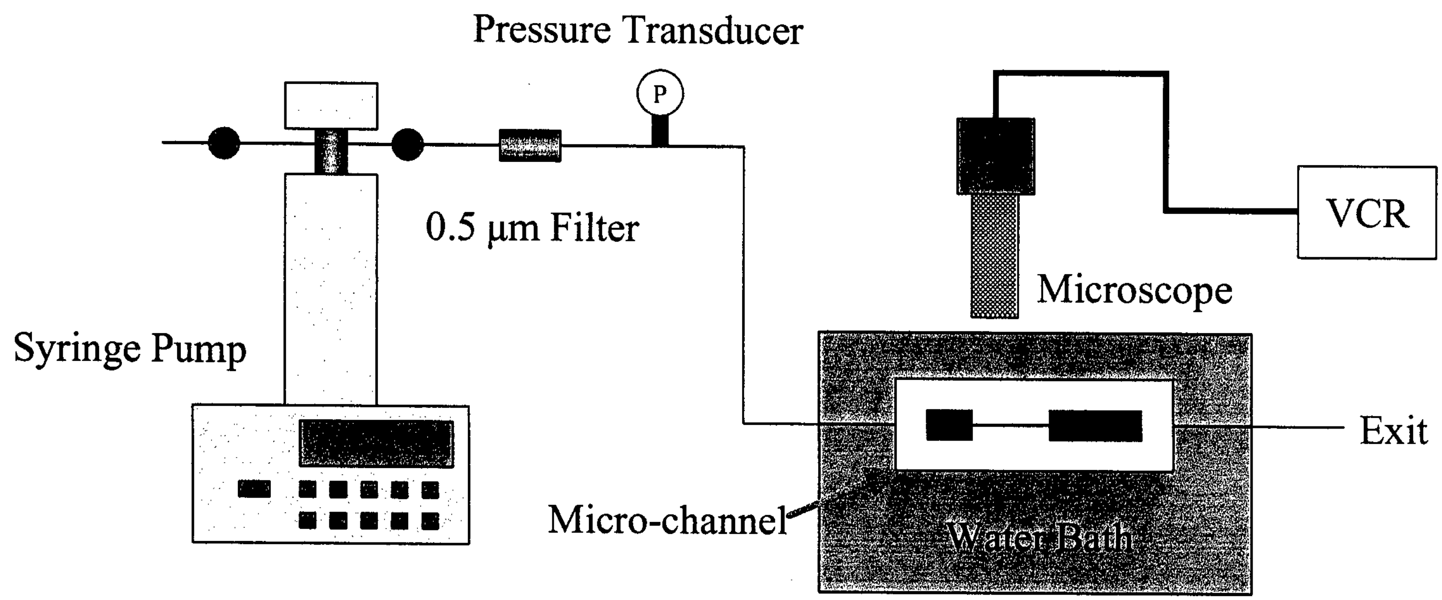
Bond Strength Measurement by Lap Shear Test

UV Curable Acrylic Adhesive (Qure Tech)



Bond strength of methylene chloride bonded joint: >300 lb (substrate failure)

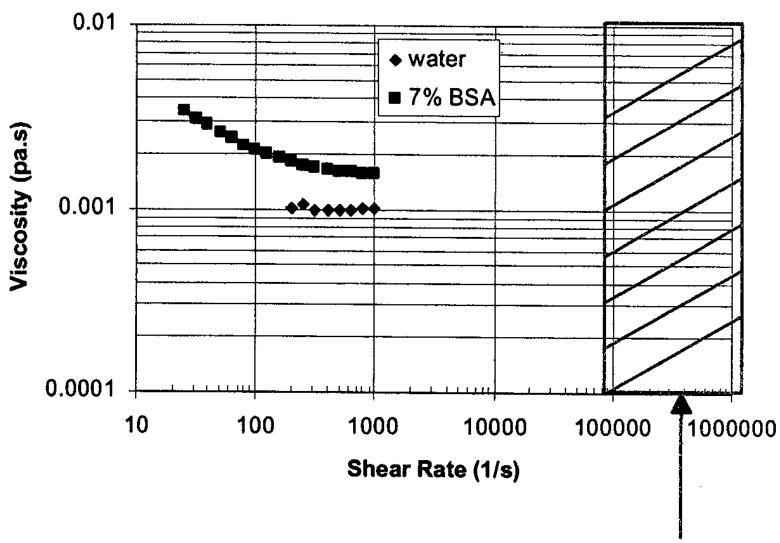
Flow in Micro-Fluidic Device



Material : Double distilled water, 7% Bovine Serum Albumin (BSA) solution, silicone oil.
Channel size : 150 & 50 μm wide, 34 μm deep; 150, 50 & 5 μm wide, 5 μm deep.
Flow rate range : 0.02~5 ml/min
Shear rate range : $10^5 \sim 2.7\times10^6$ /s
Reynolds number range : 46~1307

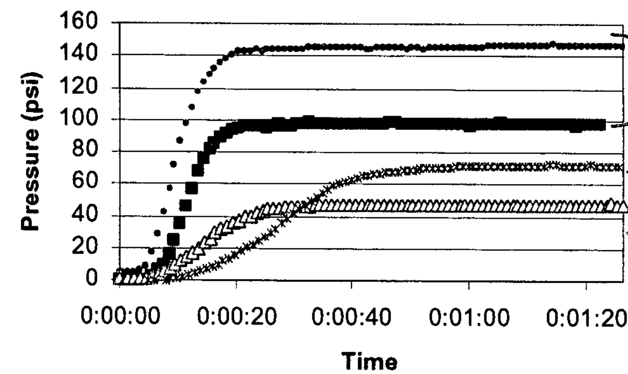
Micro-Channel Flow (steady state)

$$\frac{\mu_{BSA}}{\mu_{water}} = 1.55, \dot{\gamma} = 1000/s, T = 30^\circ C$$



Shear rate range in micro-channels

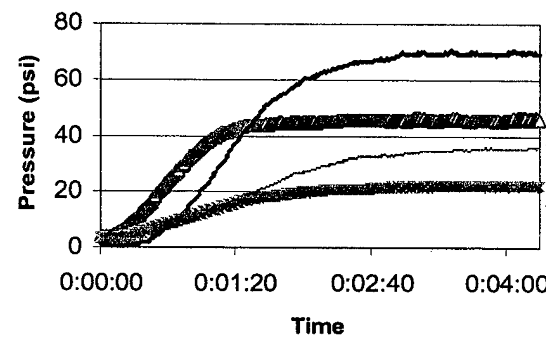
150x 34 μm channel



$$\frac{P_{BSA}}{P_{water}} = 1.52, \dot{\gamma} = 10^6/s$$

$$\frac{P_{BSA}}{P_{water}} = 1.55, \dot{\gamma} = 6 \times 10^5/s$$

50x 34 μm channel



$$\frac{P_{BSA}}{P_{water}} = 1.52, \dot{\gamma} = 3.5 \times 10^5/s$$

$$\frac{P_{BSA}}{P_{water}} = 1.59, \dot{\gamma} = 1.7 \times 10^5/s$$

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SUMMARY

•Micro-machining (master fabrication)

For microfluidic devices with structures larger than 10 micron, our work shows that CNC-machining with laser ablation of tool steel, plus vapor deposition or electroplating of chrome surface coating is well suited for the fabrication of the master (i.e. high strength, low costs, and few process steps). For smaller structures, photolithography is needed.

•Bonding

Several polymer molding techniques have been used to replicate planar microfluidic devices. Future work will concentrate on process optimization (i.e. short cycle time, low stresses, and good dimension control), 3D structures (i.e. registration of multi-layer lamination, micro injection molding and reaction injection molding), and material extension (i.e. high temperature materials like nanocomposites, PEEK, polyimide; and functional materials like hydrogels).

•Micro-flow

We are further investigating the effects of fluid rheology, fluid surface tension, and other surface forces on channel filling and saturated flow in microfluidic devices.

DARPA-ARO Workshop Microchemical Systems
16-18 June 1999
Reston, VA

Using Nanoscale Mesoporous Architectures to Design Integrated Fuel Cell Catalysts (or Pave High Surface Areas with Nanowires)

Debra Rolison, Jeffrey Long, Karen Swider Lyons, Joseph Ryan, Celia Merzbacher, Michele Anderson, Alan Berry, Veronica Cepak and Rhonda Stroud

Surface Chemistry, Optical Physics, and Surface Modification Branches

Naval Research Laboratory

Washington, DC

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Mechanistic Concerns during Direct Oxidation of Methanol On Pt(0)Ru(0) Electrocatalysts in the Direct Methanol Fuel Cell

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1. **Pt is a *great* catalyst to dehydrogenate small alkanes**

   ... but neither Pt_xRu_y bulk alloys nor Pt-Ru nanoscale blacks are superactive catalysts for MeOH oxidation

2. **H_2O dissociation on Ru(0) to form Ru-OH is accepted as the rate-determining step**

   ...confirmed for <u>bulk</u> PtRu alloy electrodes by recent spectroelectrochemical studies A. Kabbabi, R. Faure, R. Durand, B. Beden, F. Hahn, J.-M. Leger, C. M. Lamy, *J. Electroanal. Chem.* <u>444</u> (1998) 41

3. **Implicit oxidation state of mechanistic Ru-OH is Ru(I)OH**

   ...but...Conway has already taught us that Ru metal oxidizes in acid electrolyte to RuOx films at 0.2 to 0.4 V vs. NHE

   ... and these RuOx films are mixed valent Ru(III)-Ru(IV) oxides... not Ru(I)Ox S. Hadzi-Jordanov, H. Angerstein-Kozlawska, M. Vukovic, B.E. Conway, *J. Electrochem. Soc.* <u>125</u> (1978) 1471 and references within

4. **And why *does* the practical catalyst (*i.e.*, nanoscale Pt-Ru black) work best with an atom stoichiometry of one Ru for every Pt when the mechanism implies a multi-Pt surface structure?**

Mechanism of Direct Oxidation of Methanol On Pt(0)Ru(0) – Bifunctional Catalysis

1. *Electrosorption of Methanol at Pt — Oxidative Dehydrogenation*

$$CH_3OH + Pt \longrightarrow Pt\text{-}CH_2OH + H^+ + e^-$$
$$Pt\text{-}CH_2OH + Pt \longrightarrow Pt_2\text{-}CHOH + H^+ + e^-$$
$$Pt_2\text{-}CHOH + Pt \longrightarrow Pt_3\text{-}COH + H^+ + e^-$$
$$Pt_3\text{-}COH \longrightarrow Pt\text{-}CO + 2\,Pt + H^+ + e^-$$

… *but…Pt-CO difficult to oxidize at operating potential of DMFC… so…*

2. *Oxygen transfer from electrogenerated RuOH*

$$Ru + H_2O \longrightarrow Ru\text{-}OH + H^+ + e^-$$
$$Ru\text{-}OH + Pt\text{-}CO \longrightarrow Ru + Pt + CO_2 + H^+ + e^-$$

$$CH_3OH + H_2O \longrightarrow CO_2 + 6\,H^+ + 6\,e^-$$

*Accepted Wisdom #1 (How *Not* to Improve the Direct Methanol Fuel Cell)*

Nanoscale Pt-Ru blacks are bimetallic alloys because their X-ray diffraction patterns mimic those observed with bulk Pt_xRu_y alloys… in which Ru substitution into the Pt** fcc **lattice leads to lattice contraction and an observed shift of Pt peaks to higher 2θ

(1) **The "alloy" XRD pattern (*i.e.*, shifted Pt peaks) is obtained for commercial Pt-Ru blacks that have *bulk* compositions of 75% to >90% RuO_2** D.R. Rolison, P.L. Hagans, K.E. Swider, J.W. Long, *Langmuir*, 15 (1999) 774

(2) **Nanoscale Pt-Ru and its ternaries and quaternaries deviate from Vegard's law** B. Gurau, R. Viswanathan, R. Liu, T.J. Lafrenz, K.L. Ley, E.S. Smotkin, E. Reddington, A. Sapienza, B.C. Chan, T.E. Mallouk, S. Sarangapani, *J. Phys. Chem. B*, 102 (1998) 9997

— the nanoscale blacks cannot be single-phase alloys—

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Assessing the Chemical States of Pt and Ru in Nanoscale DMFC Catalysts

**BUT* as-received/as-used nanoscale Pt-Ru blacks are <u>not</u> bimetallic alloys...they consist of a mixture of metal and hydrous oxide components!*

*As shown by surface *and* bulk analyses: XPS, glow-discharge mass spec, TGA, XANES, specific capacitance*

D.R. Rolison, P.L. Hagans, K.E. Swider, J.W. Long, *Langmuir*, <u>15</u> (1999) 774

<u>Commercial Pt-Ru catalysts:</u>

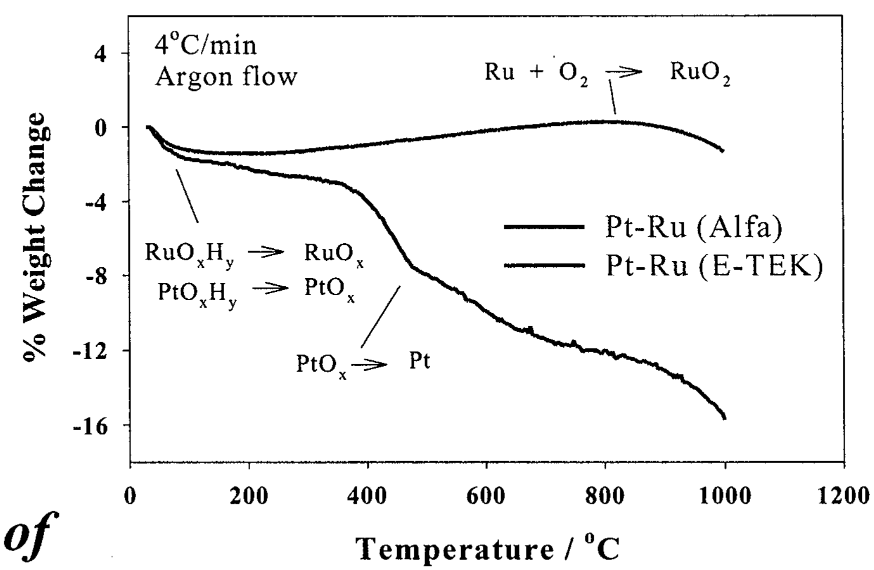
Pt-Ru (E-TEK):

$Ru^{III/IV}O_xH_y$; Pt / $Pt^{II}O_x$

Pt-Ru (Alfa Aesar):

$Ru^{III/IV}O_xH_y$ / Ru;

Pt/$Pt^{II}O_x$



TGA is a convenient method to screen Pt-Ru catalysts

The energetics that dictate structure of the Pt-Ru/ionomer interface in the MEA are those of MO_xH_y *not* M

How does the presence of RuOxHy in Pt-Ru nanoscale blacks affect the catalytic activity of methanol oxidation??

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- ***Compositionally and mechanistically hydrous RuOx should be far more beneficial for direct MeOH oxidation than Ru metal***
  - **WHY?** Hydrous RuO*x* innately expresses Ru-OH speciation *and* is a mixed electron and proton conductor

    i.e., **RuO*x*H*y* exhibits pseudocapacitance:**

$$RuO_x(OH)_y + \delta H^+ + \delta e^- \leftrightarrow RuO_{x-\delta}(OH)_{y+\delta}$$

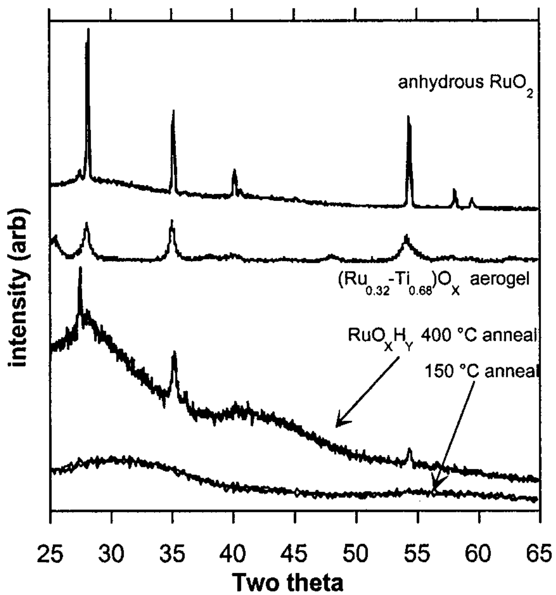
$$Ru^{IV}\text{—}\ O^{2-} + H^+ + e^- \leftrightarrow Ru^{III}\text{—}\ OH^-$$

  - Specific capacitance (F/g) relates to:
    - **Ru-OH content (degree of hydration)**
    - **Proton conductivity**
  - known that Pt and Ru in PtRu alloys segregate under open-circuit conditions (in dilute H_2SO_4) $\Rightarrow$ RuO*x* forms

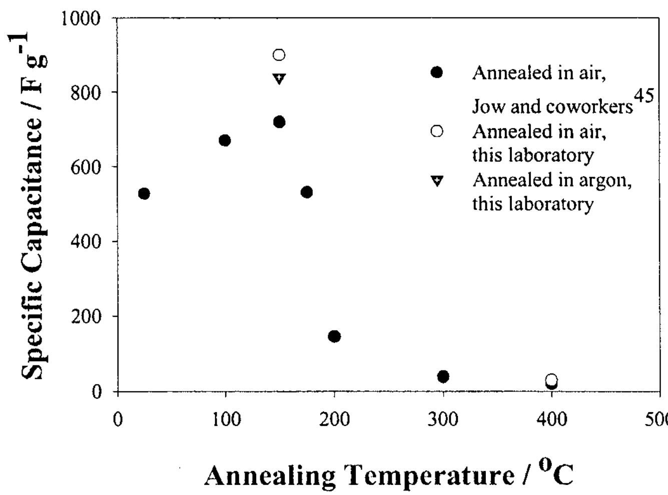
E. Ticanelli, J.G. Beery, M.T. Paffett, S. Gottesfeld, *J. Electroanal. Chem.* 258 (1989) 61

RuOx: Bulk Disorder Correlates with Pseudocapacitance

the more 3D rutile...
the fewer F/g stored



Sample	Specific Capacitance / (F/g)
$RuO_2 \cdot 0.5\ H_2O$	900
$RuO_2 \cdot 0.03\ H_2O$	29
$(Ru_{0.32}\text{-}Ti_{0.68})Ox$ aerogel	2.3
anhydrous RuO_2	0.75



⇨ **Degree of hydration is critical!**

—Heating above 175 °C crushes H^+ conductivity/charge storage

(•) J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699

(o) J.W. Long, K.E. Swider, C.I. Merzbacher, D.R. Rolison, *Langmuir*, 15 (1999) 780

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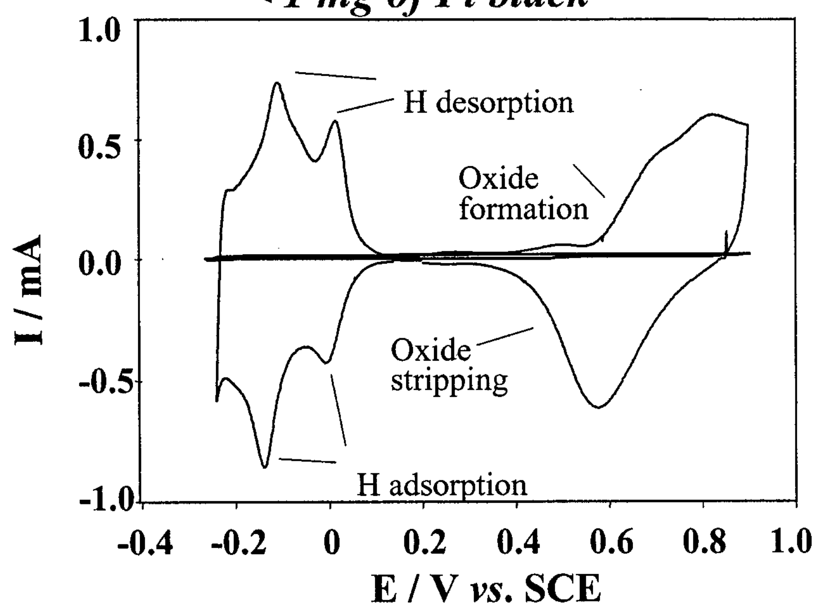
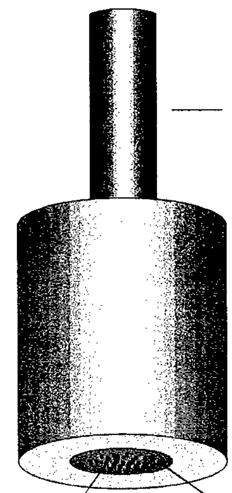
Understanding the Innate Electrochemistry of High Surface Area Electrocatalysts

- **Conductive carbon/wax composite, "sticky carbon"— acetylene black and beeswax [~35:65 wt/wt]**
- **Powder of interest (aerogel or Pt-Ru black or RuO_2 standard) is addressed by pressing a known mass into the sticky electrode surface**

< 1 mg of Pt black





* Y.-F. Yang, Y.-H. Zhou, C.-S. Cha, *Electrochim. Acta* 40 (1995) 2579
* J.W. Long, D.R. Rolison in *New Directions in Electroanalytical Chemistry II*, 99-5, ECS, 1999, 125

Benefits of sticky carbon method for high surface area materials

- ***< 1 mg of material required***
- ***quantitative electroanalysis***
- ***avoid problem of large RC time constants due to large surface areas***
- ***no solvents, no polymer binders***

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Voltammetry as a Function of Treatment of Pt-Ru Blacks: If RuOxHy is Present, so is Pseudocapacitance in Acid Electrolyte

- **Voltammetry at nanoscale Pt-Ru catalysts is dominated by large pseudocapacitance, consistent with presence of RuO_xH_y species:**

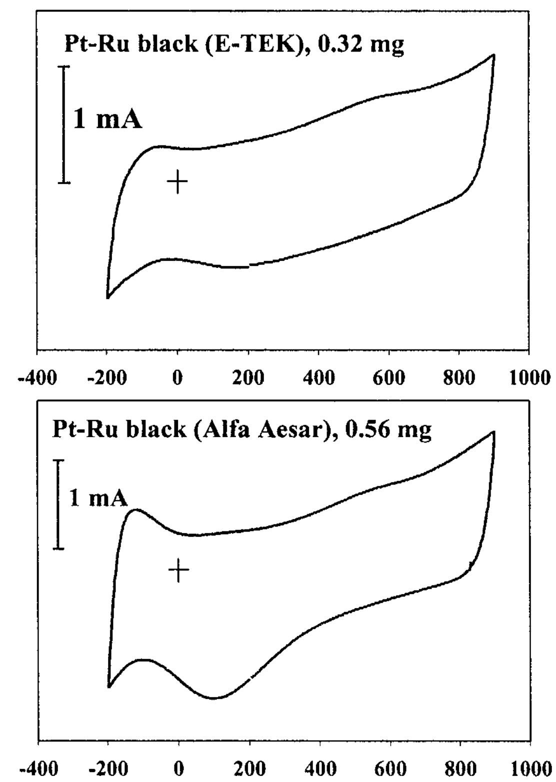
$$RuO_x(OH)_y + \delta H^+ + \delta e^- \rightleftharpoons RuO_{x-\delta}(OH)_{y+\delta}$$

	Specific Capac. (F/g)	BET Surface Area (m^2/g)
Pt-Ru (E-TEK)	650	105
Pt-Ru (Alfa Aesar)	530	68

Is the presence of adventitious RuOxHy beneficial for methanol oxidation catalysis?

- **Mixed H^+/e^- conductor**
- **Inherent Ru-OH speciation**
- **Efficient H_2O dissociation**

1 M H_2SO_4, 5 mV/s



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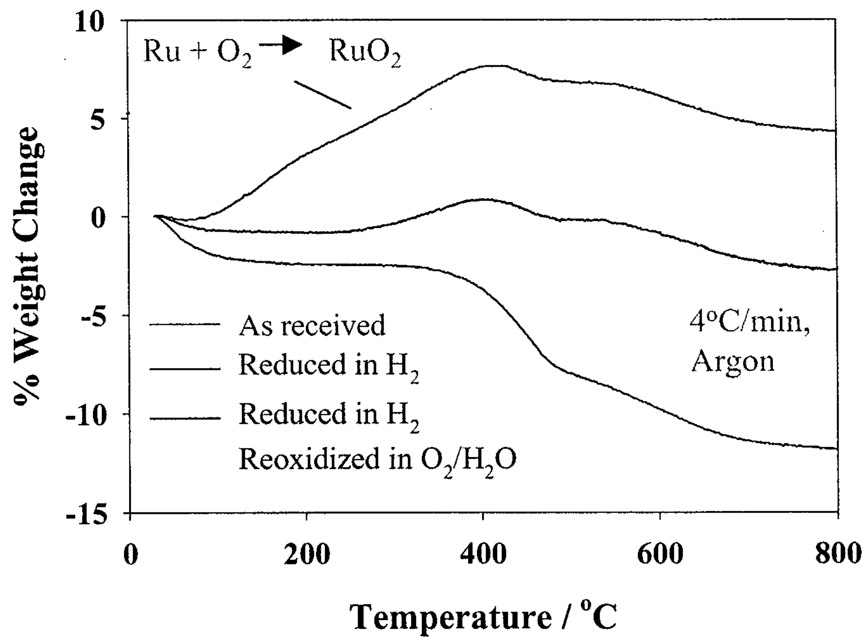
Controlling the Chemical States in Nanoscale Pt-Ru

- **Can the chemical state of Ru be controlled in nanoscale Pt-Ru?**

$$\mathbf{RuO_xH_y} \underset{O_2/H_2O}{\overset{H_2}{\rightleftharpoons}} \mathbf{Ru}$$

Yes, by a combination of T and atmosphere!



1. ***Reduction of Pt-Ru:***

   ✦ 2 h / 100 °C / 10% H_2

   Almost complete conversion of RuO_xH_y to Ru metal

2. ***Re-oxidation of reduced Pt-Ru:***

   ✦ 20 h / 100 °C / humidified O_2

   ~80% of Ru metal converted back to RuO_xH_y

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*Accepted Wisdom #2 (How *Not* to Improve the Direct Methanol Fuel Cell)*

Pt-Ru blacks may/probably have surface oxides, but these are reduced once exposed to methanol, especially under the operating conditions of the DMFC

(1) Yes, commercial (or in-house) Pt-Ru blacks have surface PtO_x and RuO_x, but they have enough analyzed oxygen present to have *bulk* compositions of 75% to >90% RuO_2

D.R. Rolison, P.L. Hagans, K.E. Swider, J.W. Long, *Langmuir*, 15 (1999) 774

(2) Hydrous RuO_x is chemically durable (more so than anhydrous RuO_2) — RuO_xH_y cannot be electrochemically reduced — commercial Pt-Ru blacks retain RuQ during operation of a MeOH-fed fuel cell

EXAFS results: J. McBreen, S. Mukerjee, *J. Electrochem. Soc.* 142 (1995) 3399
XANES results: K.E. Swider, K.I. Pandya, A.D. Kowalek, P.L Hagans, W.E. OGrady , Extended Abstracts, 95-1, 188th Meeting of the Electrochemical Society, Reno, NV, 1995

State of Pt in Nanoscale Pt-Ru as a function of Treatment— Open Circuit Potential Predicts the Activity of the Pt for MeOH oxidation

- How does presence of PtO_x affect methanol oxidation activity?
- How does MeOH at T > ambient affect PtO_x?

1 *M* MeOH + 1 *M* H_2SO_4

Pt-Ru (E-TEK)	E_{oc} *vs.* NHE
As-received	+695
As-received, conditioned at E = 70 mV	+390
Reduced in H_2 /100 °C	+315
Reduced in H_2, Re-oxidized in O_2/H_2O	+394
Pt-Ru (Alfa Aesar)	+348

Pt-Ru, as-received

T / °C	E_{oc} / (mV) *vs.* NHE
25	+744
35	+744
45	+295 (~10 min)
55	+238

PtOx reduced by MeOH at T ~ 45 °C

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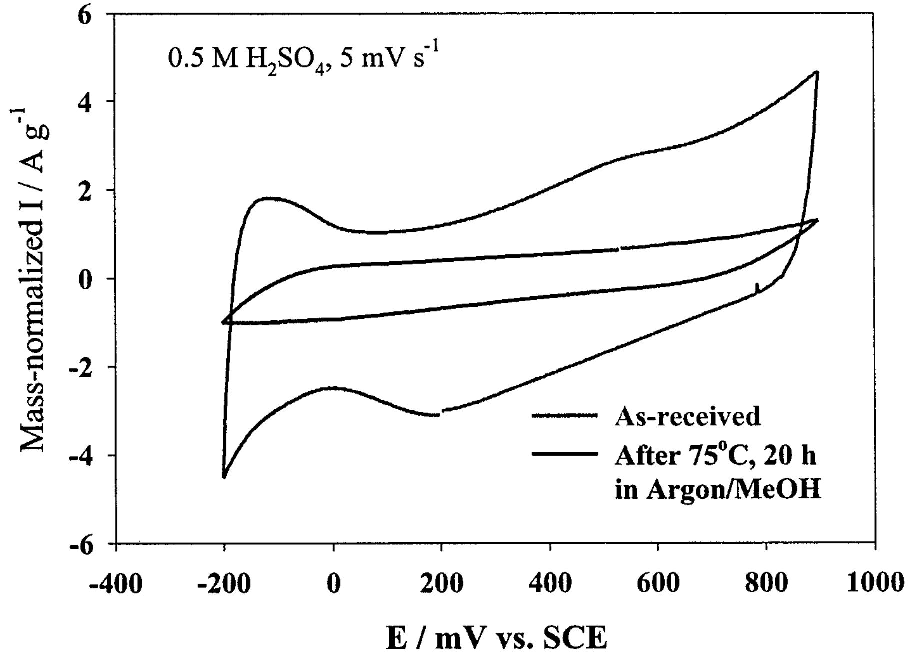
State of Ru in Nanoscale Pt-Ru after Exposure to MeOH / T – Pseudocapacitance Indicates the Chemical State of the Ru



Pt-Ru (E-TEK)	Spec. Cap.
As-received	650 F g^{-1}
After 75 °C, 20 h in Argon/MeOH gas flow	190 F g^{-1}

The nanoscale black is affected by gas-phase treatment with MeOH at 75 °C, but remains highly capacitive and does not develop the faradaic features indicative of Ru metal… dehydrates during treatment with argon/MeOH

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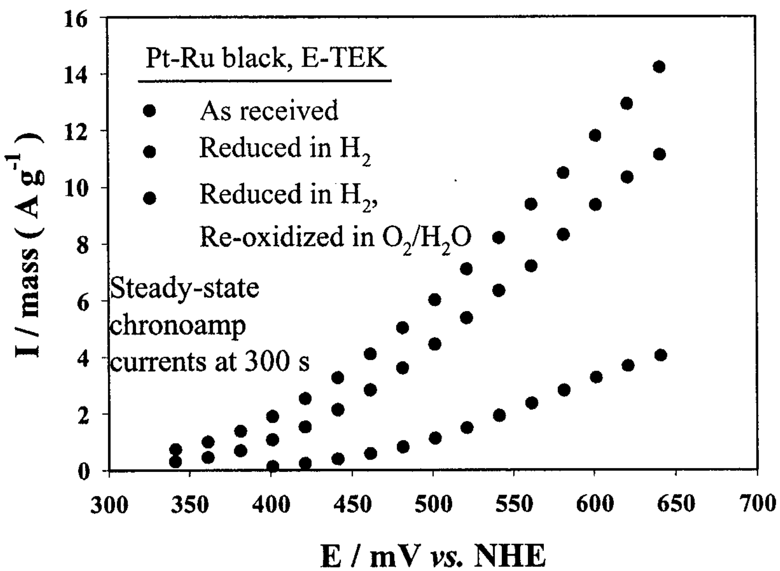
Accepted Wisdom #3 (How *Not* to Improve the Direct Methanol Fuel Cell)

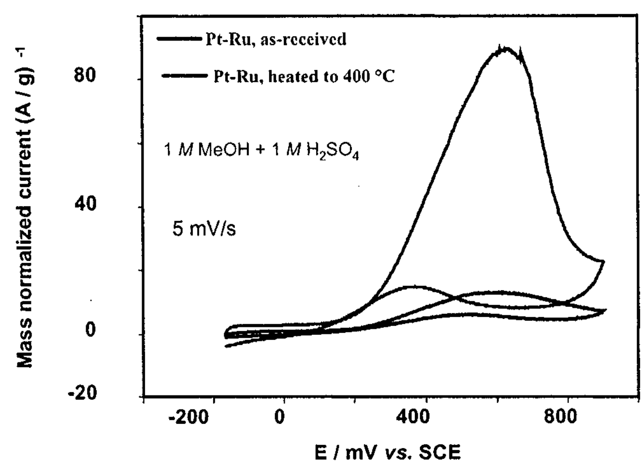
Pt-Ru blacks are catalytic for direct MeOH oxidation as bimetallic alloys

...*but*... Pt-Ru blacks reduced in H_2 at temperatures consistent with MEA fabrication or fuel cell operation are active only compared to Pt black...

1 *M* MeOH + 1 *M* H_2SO_4
500 rpm, 25 °C



Pt-Ru E-TEK	BET Surface Area
As-received	105 $m^2\ g^{-1}$
Reduced in H_2	70 $m^2\ g^{-1}$



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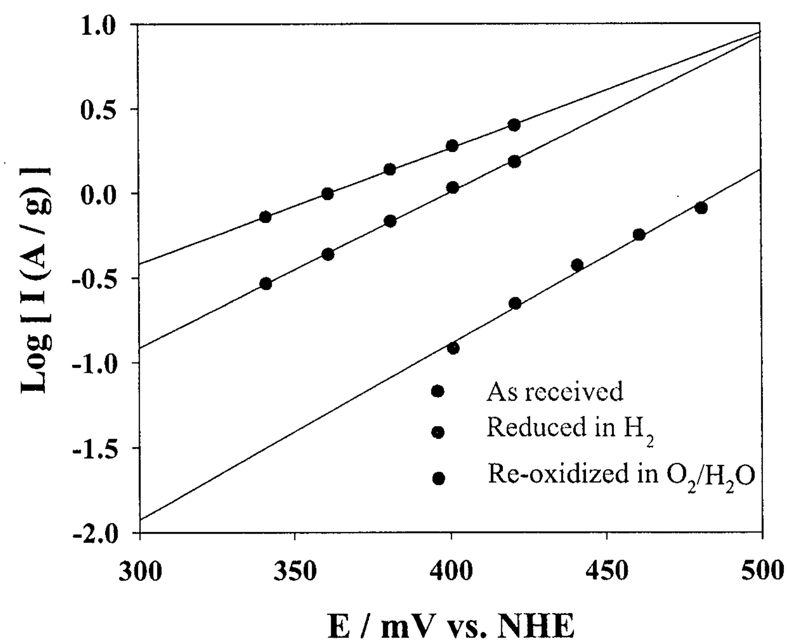
*Accepted Wisdom #4 (How *Not* to Improve the Direct Methanol Fuel Cell)*

Have Ru-OH...have activity for direct MeOH oxidation

... yes*.but*... the bulk conversion of Ru to $RuQH_y$ affects the exchange current density, *i.e.*, the **bulk** structure of the RuO_xH_y component of Pt-Ru blacks appears to control the heterogeneous rate constant...

	Tafel Slope (mV/dec)	I_0* (mA/g)
As-received	140	5.5
Reduced in H_2	100	0.019
Re-oxidized in O_2/H_2O	110	0.41

* *Based on $E^o = 0.03$ V vs. NHE*



☞ **Tafel slopes consistent with a 1 e^- r.d.s.**

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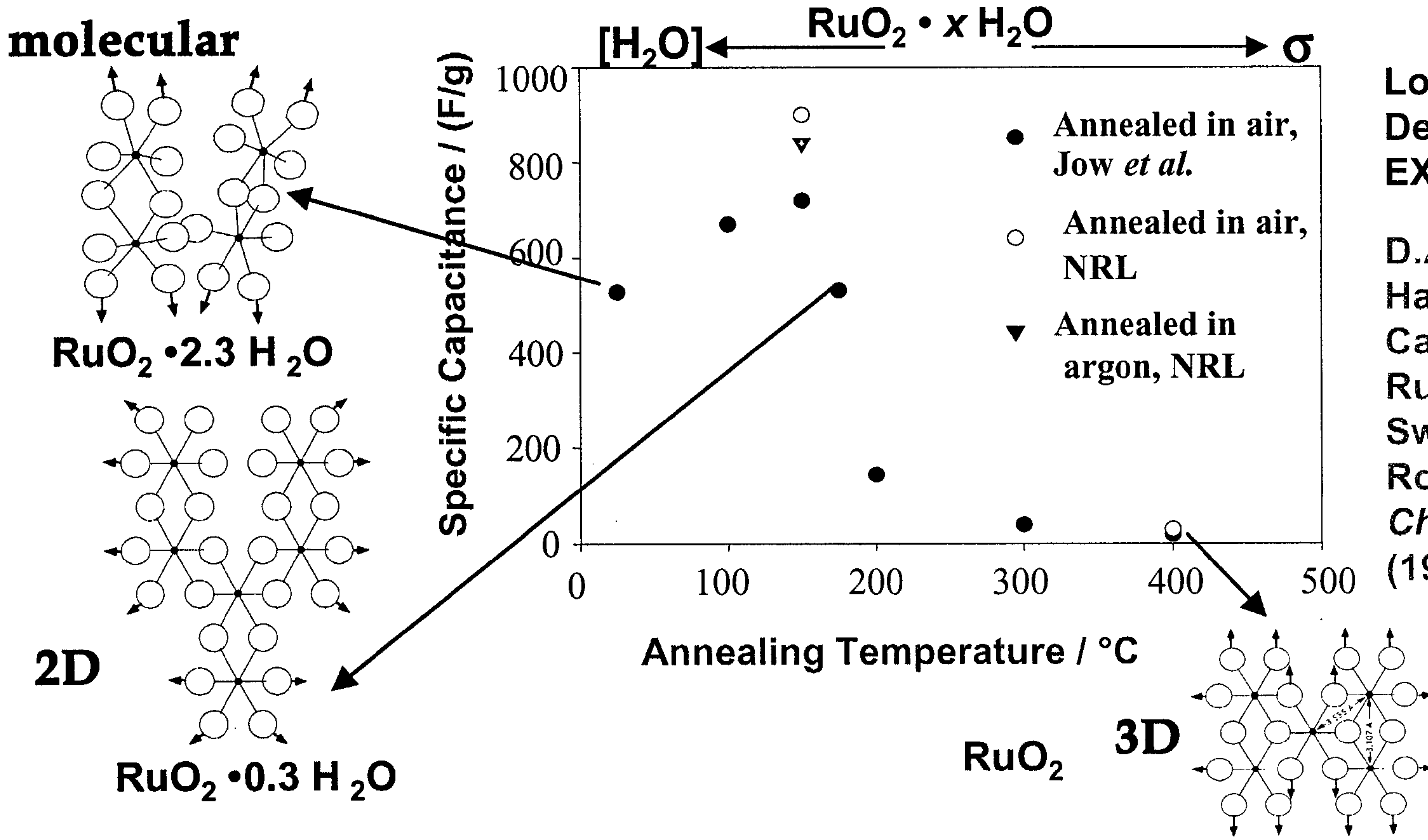
What is Bulk Hydrous RuOx Structure Good For???

... high specific capacitance... therefore effective H^+ conductivity $RuO_2 \cdot 0.5\ H_2O$ is the composition that yields optimal charge storage— this composition is amorphous by XRD



Local Structures Determined by EXAFS Analyses:

D.A. McKeown, P.L. Hagans, L.P.L. Carette, A.E. Russell, K.E. Swider, D.R. Rolison, *J. Phys. Chem. B*, 103 (1999) in press

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*How *to* Improve the Direct Methanol Fuel Cell: Conclusions*

Nanoscale Pt-Ru black catalysts are <u>not</u> bimetallic alloys, but consist of a mixture of metal and hydrous oxide components

- *PtOx is reduced by T/MeOH; RuOxHy is a sturdier beast*

The chemical states of Ru and Pt can be manipulated by temperature/atmosphere under relatively mild conditions

The RuO*x*H*y* speciation of Ru affords a much more active catalyst for methanol oxidation than Ru metal

- *Optimal form of Pt-Ru catalyst is Pt metal and RuOxHy*

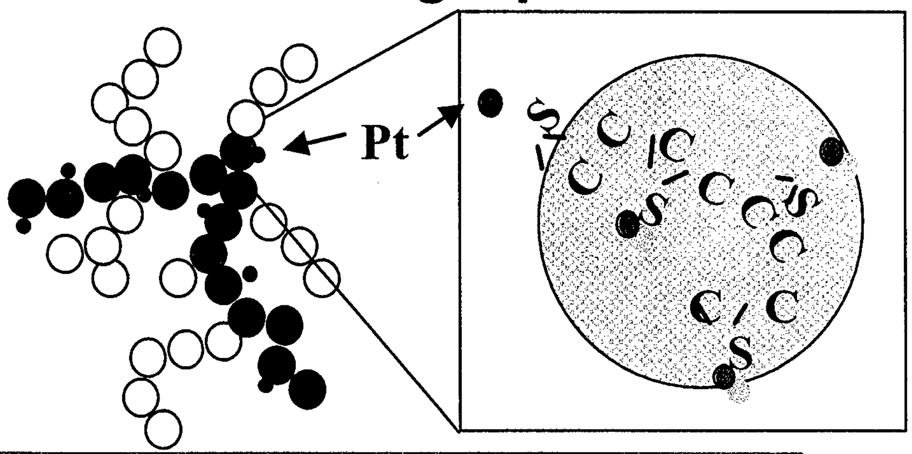
*Preliminary indication that surface termination in Ru-OH is necessary but not sufficient for catalytic activity — *bulk* RuOxHy structure must be optimized to achieve high proton conductivity*

Computations on the structure-H^+ conduction properties of amorphous hydrous oxides are required

Combinatorial efforts may help find the elements that stabilize optimally H^+-conductive structures of RuOxHy

Design of an Integrated Direct Methanol Fuel Cell Electrocatalyst

- **Understand the pieces**
- **Integrate fuel-cell materials within an aerogel platform**



With ~40 mg/mL of Vulcan C in SiO_2 sol…base-catalyzed aerogel composite is conductive (MΩ resistance)...acid-catalyzed aerogel composite is not conductive (even at >> higher ρ_s)

Thiophene-like sulfur in Vulcan carbon self-assembles noble metal particles, including Au or Pt colloids of known size

➤ **Hydrous RuO_x can be electrolesslyplated onto Pt metal from $RuCl_3$ solutions**

Chrzanowski, Kim, Wieckowski, *Catal. Lett.* **1998**, *50*, 69

Pt-RuO_xH_y catalysts dispersed onto carbon (acting also as a current collector), while the mesoporous architecture of the aerogel permits ready access of MeOH to all electrocatalyst particles

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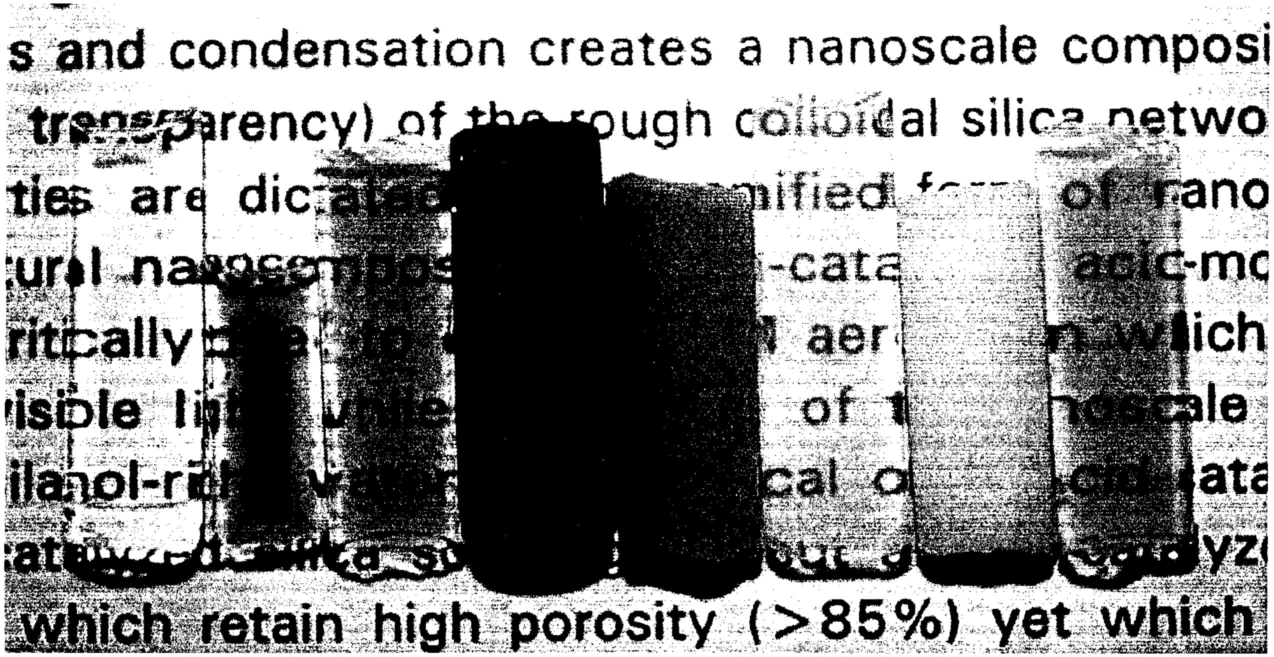
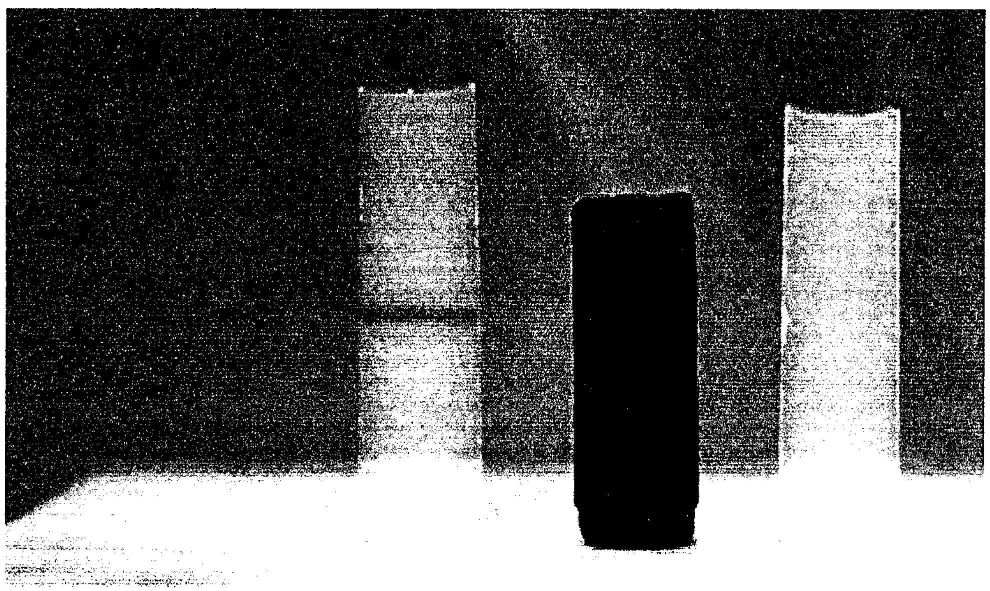


Silica-based composite aerogels (from left to right): SiO_2; **colloidal Pt-SiO_2**; **colloidal Au-SiO_2**; **Vulcan carbon-SiO_2**; **$Fe^{II}(bpy)_3NaY$-SiO_2**; **$TiO_{2\,(aerogel)}$-SiO_2**; **Degussa titania-SiO_2**; and **PMMA-SiO_2**



Preparing Black Materials from Being and Nothingness: He-Ne laser (from right) irradiating air, SiO_2 aerogel, and **Vulcan carbon-SiO_2**; no light is transmitted through the C-SiO_2 composite aerogel, even though it is 80% open space.

C.A. Morris, M.L. Anderson, R.M. Stroud, C.I. Merzbacher, D.R. Rolison, *Science* 284 (1999) 622

*Aerogels = Composites of Being and Nothingness**

* J.-P. Sartre, "*LÊtre et le Néant* ", Gallimard: Paris, 1943.

ATTRIBUTES

High surface area
— *100-1000 m^2/g*

Low density
— *0.002 - 0.30 g/cm^3*

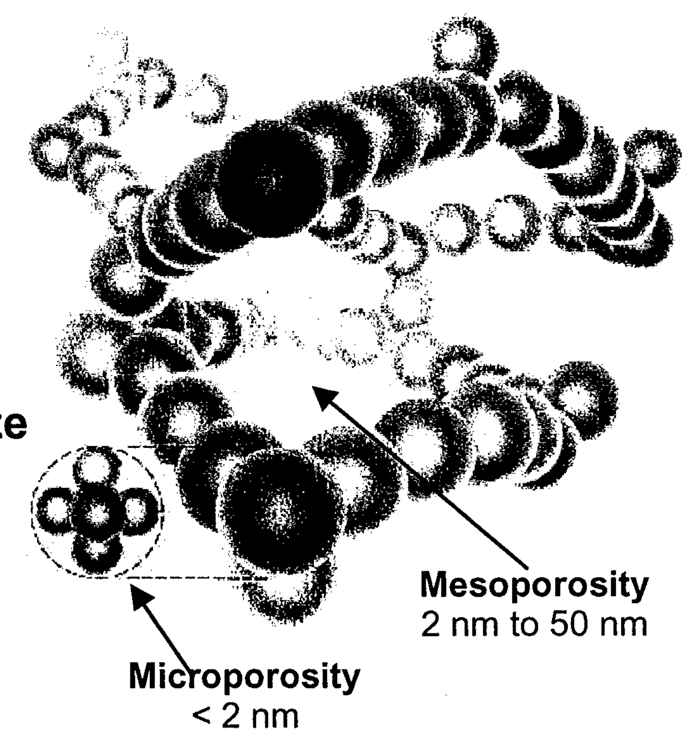
High porosity
— *75 - 99% porous*

Nanoscale particle size

Prepared by sol-gel chemistry/SCF drying

Amorphous to x-ray

Contains both meso- and microporosity



APPLICATIONS

Highly porous host/storage materials

Thermal superinsulators

Mesoscopic filtration

Cherenkov radiation detectors

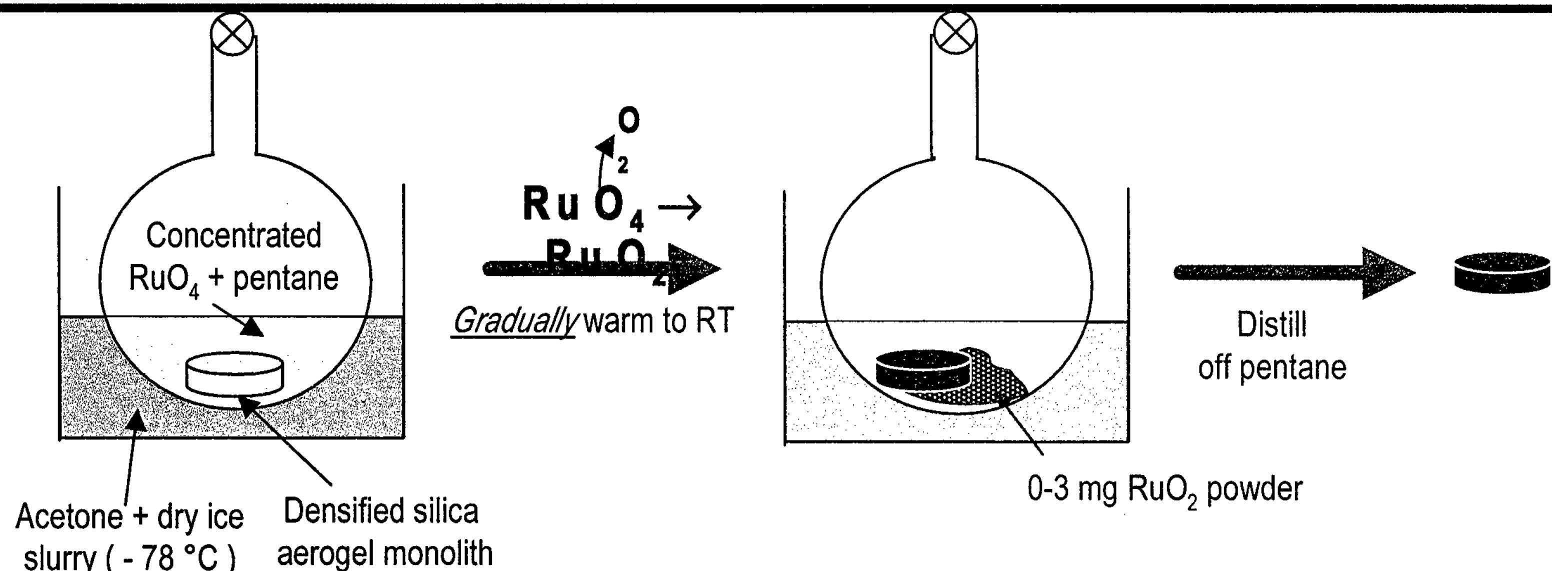
Passive solar heating

Catalysis
- ***sinter-resistant***
- ***enhanced performance***

Supercapacitors

Low Temperature Deposition of RuO_2 on Silica Aerogel

Ru precursor = RuO_4 — m.p.= 27 °C; b.p. = 129 °C; stable in pentane solution



	ΔWt%	Conductivity (μS/cm)	Molar Surface Area (10^4 m^2/mol)	Ave Pore Diam. (nm)	Molar Pore Volume (cm^3/mol)
Uncoated SiO_2 (500 °C)	–	–	5.1	14.5	184
Uncoated SiO_2 (900 °C)	–	–	3.0	11.8	100
as-dep. RuO_2 on SiO_2 (900 °C)	50-75	1-10	3.2	12.4	100
RuO_2 on SiO_2 (O_2 annealed)	50-75	~10,000	3.3	12.3	110

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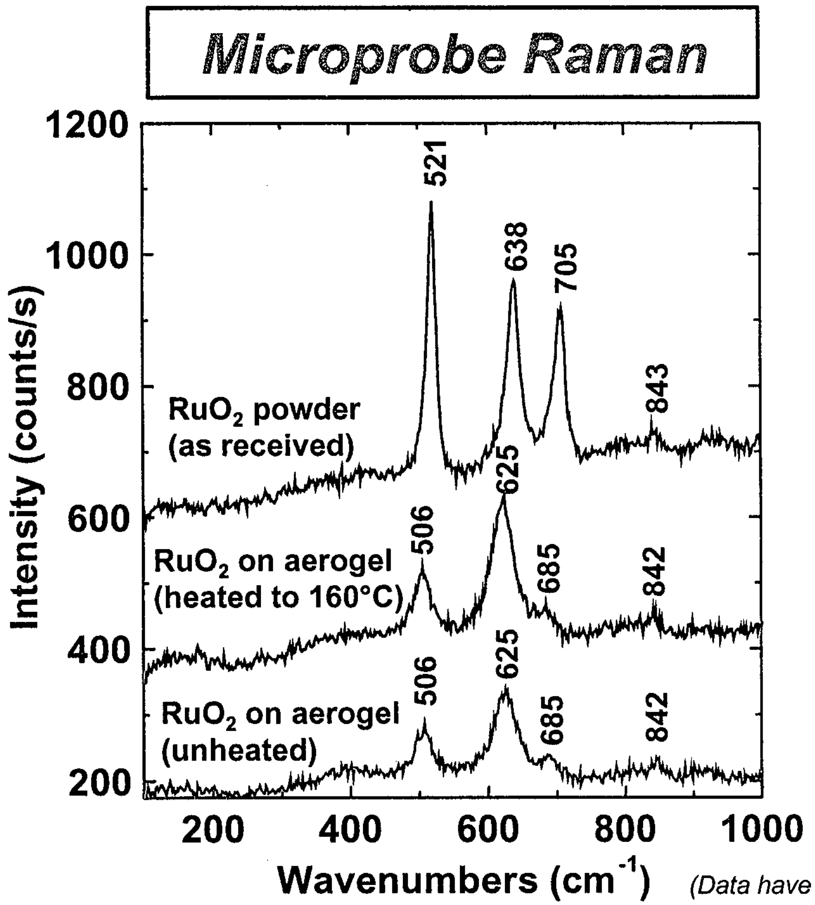
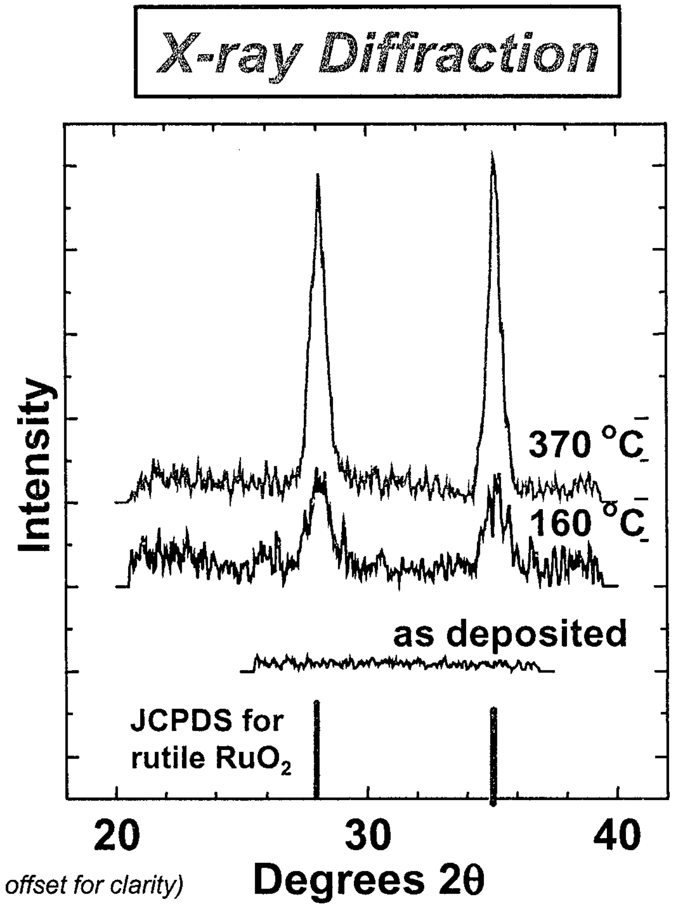
Is the Deposited Material RuO_2 ??— Yes



(Data have been offset for clarity)



- ...as-deposited material is RuO_2, but not 3-D crystalline rutile RuO_2

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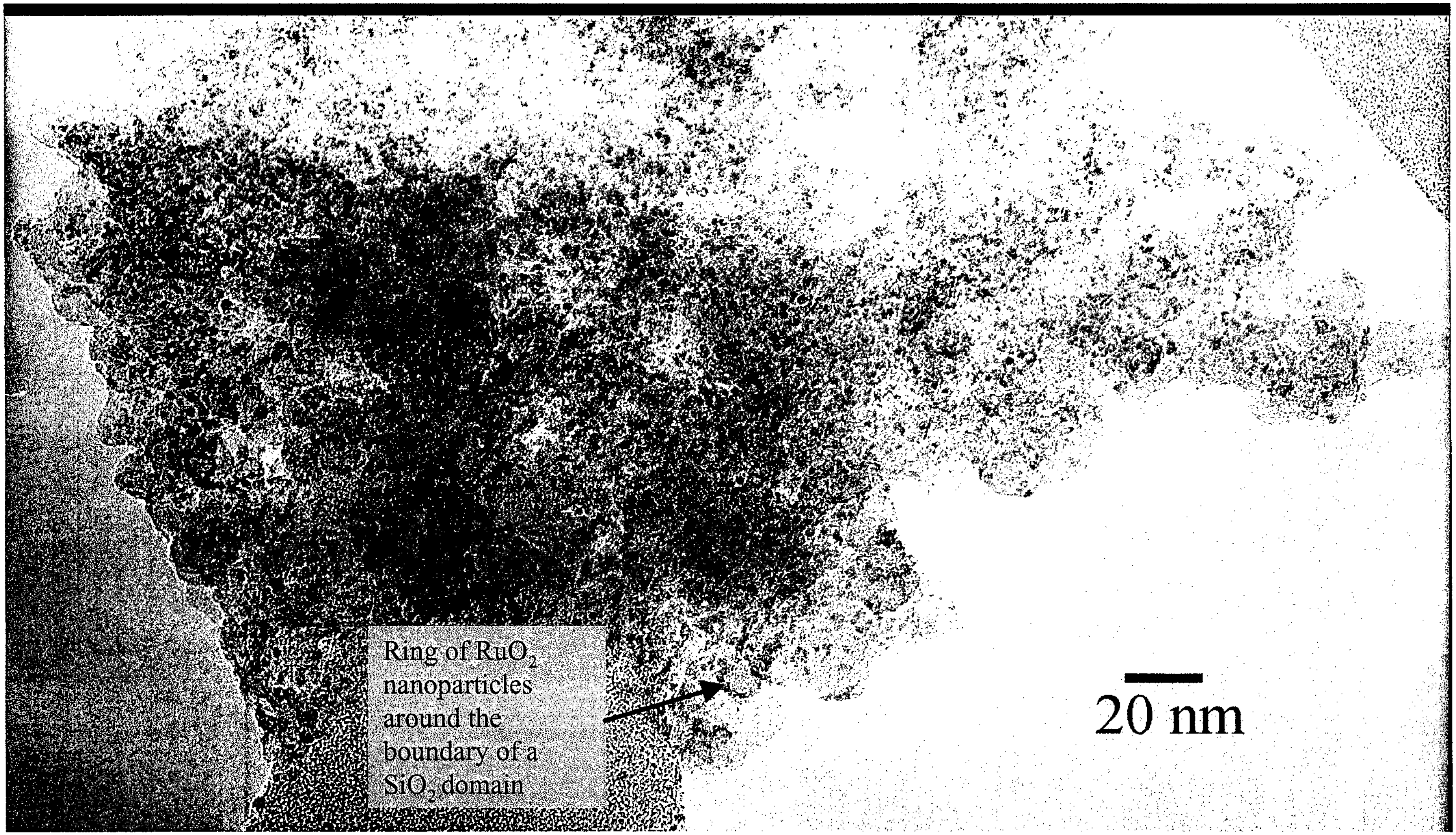
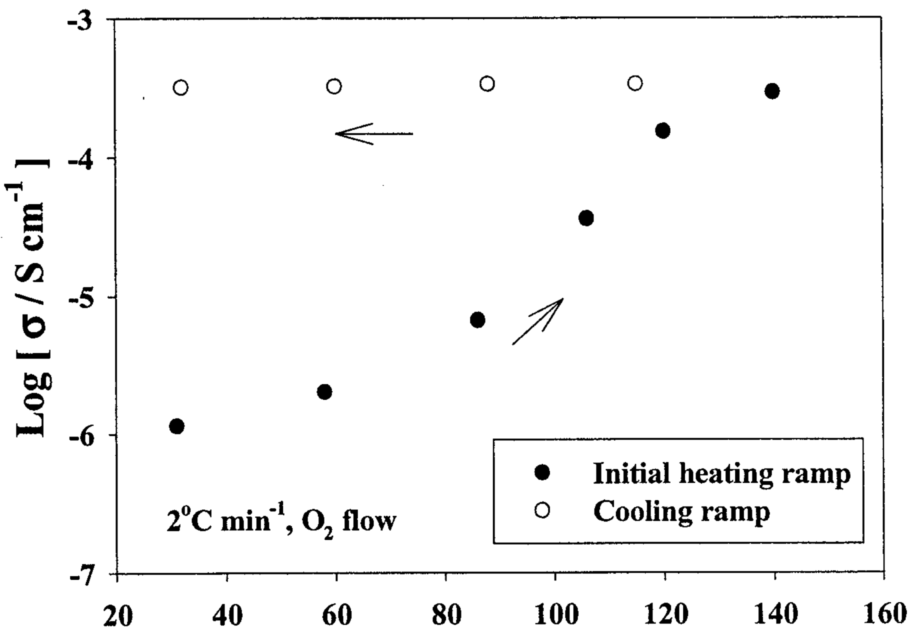
As-deposited RuO_2 on Silica Aerogel: *Wiring an Insulating High Surface Area Topology*



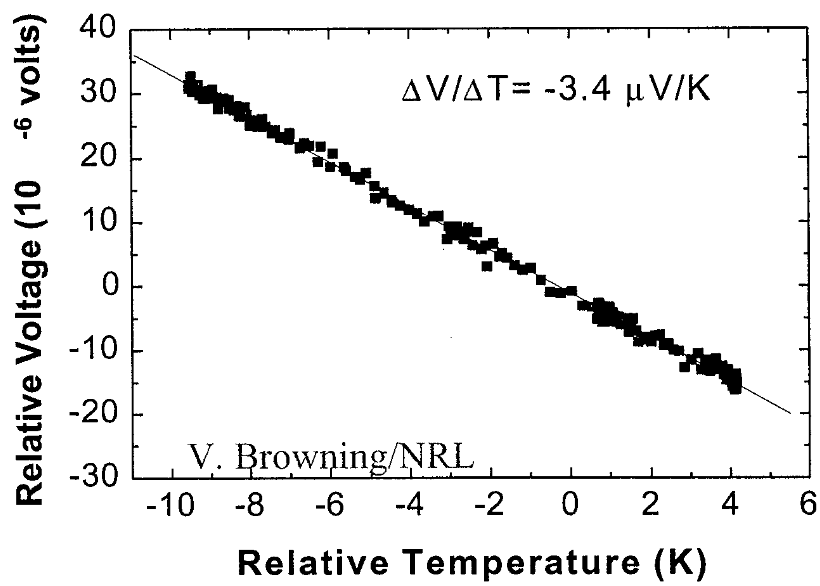
TEM/Rhonda Stroud/NRL(6370)

Electrical Properties of Nanoscale RuO_2 Deposited on Silica Aerogel

Conductivity as a function of low T annealing in oxygen



Thermopower



- ✦ >100*x* durable improvement in conductivity after heating in flowing O_2 to ~150 °C
- ✦ Seebeck coefficient consistent with metallic conductor

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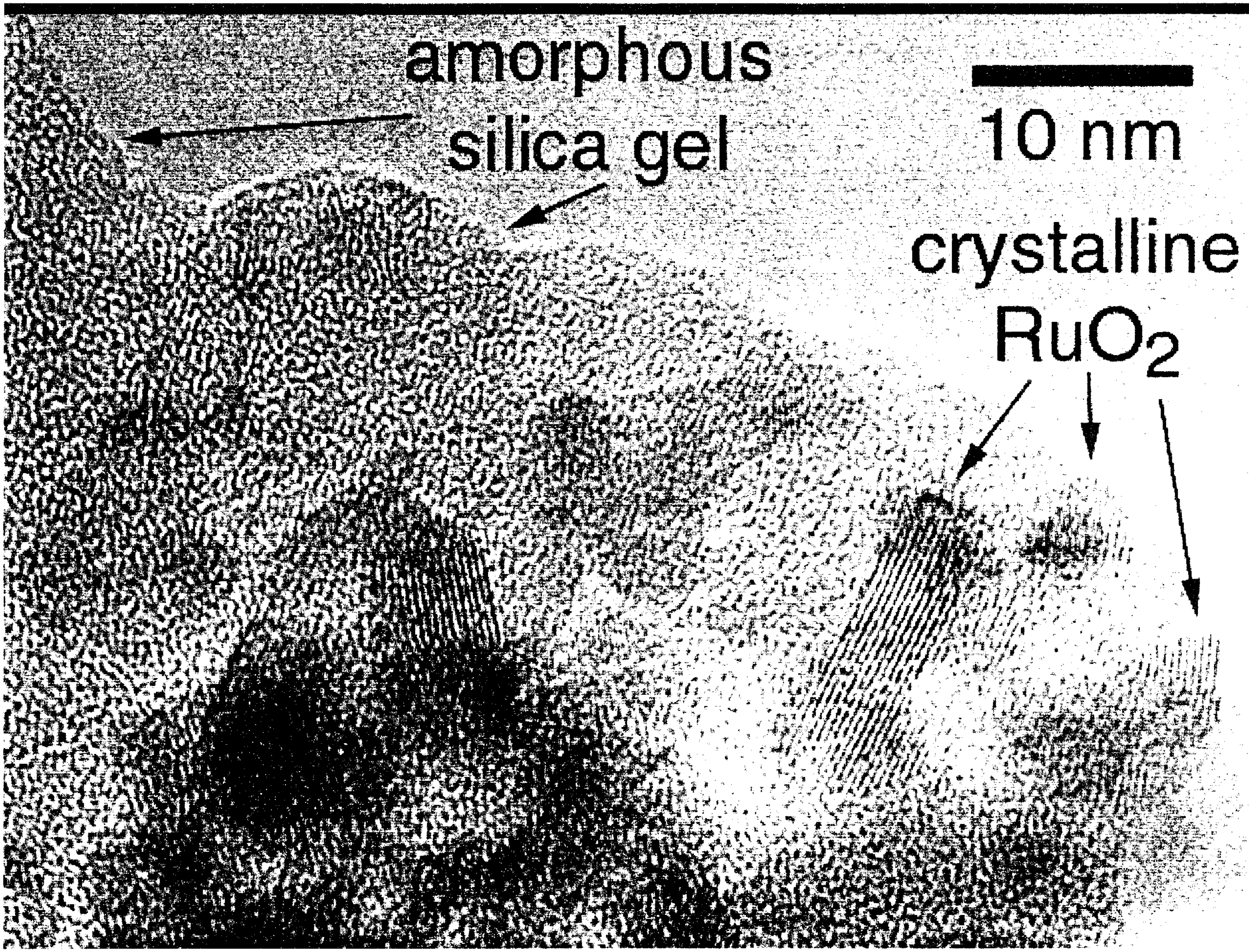
Crystallizing a Nanowire—RuO_2 after O_2 Anneal



Lattice spacings consistent with rutile RuO_2

TEM Rhonda Stroud NRL (6370)

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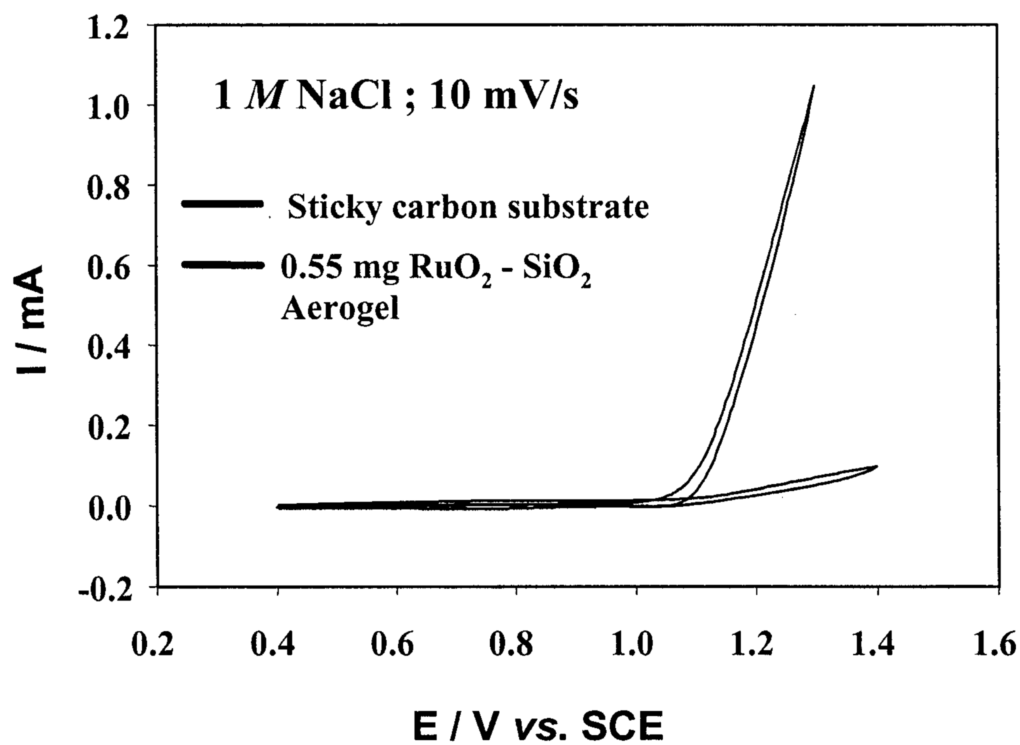
Electrochemical Properties of Nanoscale RuO_2 Deposited on Silica Aerogel

nano-RuO_2 provides a massively parallel cobweb of electrical wiring through the silica aerogel ... but is it an electrochemical material???

✦... ***oh, yeah ... electrocatalytic for brine electrolysis***



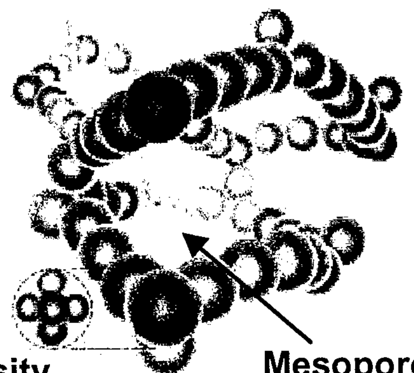
Summary

- **Intrinsic properties of aerogels** *(nanoscale, mesoporous, high surface area, networked)* **make them designable architectures for next-generation electrical materials, sensors, catalysts...**
- **Nanoscale particles of crystalline RuO_2 have been deposited on SiO_2 aerogel by a novel sub-0°C synthesis** ... *as contrasted to thermal decomposition (T>100 °C) of standard Ru precursors ($Ru_3(CO)_{12}$; $Ru(acac)_3$; ruthenocene) which yields low weight uptakes, non-conformal (ball) morphologies, non-conductive composites*
- **RuO_2 / SiO_2 nanocomposites show:**
  - » metallic conductivity throughout (up to 0.01 $S cm^{-1}$)
  - » high porosity (~75%)
  - » aerogel structure of nanoparticles connected in open network
- **"Cobweb" of low dimensional RuO_2 nanowires leads to parallel wiring ∴ appreciable end-to-end conductivity of the macroscopic, mesoporous SiO_2 monolith**

NRL Surface Chemistry-Optical Physics [$$: DARPA/ONR/NRL]

Aerogels—Composites of Being and Nothingness

pearl necklace model of silica aerogels



Research Team

Debra Rolison; Celia Merzbacher - Team Leaders

Karen Swider; Jeffrey Long; Michele Anderson; Veronica Cepak, Jeremy Pietron

— Post-Doctoral Associates

Alan Berry; Rhonda Stroud — NRL Staff

John Barker — NIST

Nicholas Leventis, John Fontanella

— ASEE Summer Faculty

Catherine Morris, Lala Qadir, Chris Sharp, Joseph Ryan, Michelle Korwin, Zack Holmrigaus

— Undergraduate Researchers

Scientific Approach

- **Synthesize new aerogel compositions**
- **Synthesize composite aero~~gels~~**-use silica sol to glue any particulate suspension (nm to mm in size)
- **Characterize with a spectrum of analytical and materials science techniques**
- **Investigate electrical, electrochemical, sensor, catalytic, thermoelectric, and optical properties**

Research Objectives

- **Stabilize nanoscale matter into a macroscopic, networked structure with inherently rapid molecular mass transport through mesopores**
- **Break limitations imposed by bulk/ homogeneous matter on various physicochemical properties**

Technical Payoff

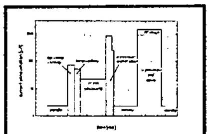
- **Low weight platforms for power sources, thermoelectric materials, and sensors**
- **Temperature-stable, sintering-resistant platforms for catalysis and power sources**
- **Blend bulk/surface character for new optical, electrochemical, sensing materials**

Microbatteries for use with MEMS Devices

J.N. Harb (Brigham Young University), R.M. LaFollette (Bipolar Technologies Corporation),
J. D.Holladay, P.H. Humble, L.G. Salmon [4], R.A. Barksdale, and B.A. Anderson (Brigham Young University)

MEMS

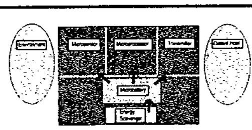
- Integrated devices designed to interact and communicate with the physical world. Commonly known as micromachines
- Applications: accelerometers, pressure sensors, chemical sensors, movement sensors, flow sensors, micro-optics, and optical scanners.
- Target Systems: remote autonomous MEMS devices.



MEMS Device Duty Cycle [1]

Target Values

- Area 0.1 cm^2
- Capacity : > 2 C/cm^2
- Power: > 5 $mWcm^2$
- Cell Voltage: > 1.2 V
- Secondary Battery
- Integrable



Microbattery, Energy Conversion Device and MEMS Microsensor Device Concept.

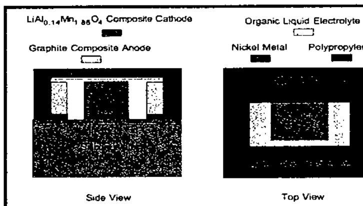
This poster describes batteries that have been developed to satisfy the power and energy needs of remote autonomous MEMS based on anticipated duty cycles. Such cycles involve short "high-power" pulses (e.g., for acquisition or communication) superimposed on low stand-by power. Batteries may be recharged during the low-power portions of the cycle by scavenging energy from the environment (e.g., via solar panels).

Our efforts to date have been focused on Ni/Zn microcells with an aqueous KOH electrolyte, and on lithium-ion microcells with a liquid organic electrolyte. All cells are made with high-volume low-cost integrated circuit (IC) fabrication techniques.

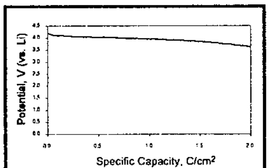
The Ni/Zn electrochemical couple was chosen for its high power density and other favorable characteristics. The NiOOH positive electrode provides flexibility since this electrode can be used with a variety of different negative electrodes, and can be fabricated in either the charged or discharged state. Use of zinc as the negative electrode provides a high specific capacity.

The Li-ion cells utilize synthetic graphite anodes and $LiAl_{0.14}Mn_{1.86}O_4$ [2] cathodes. They offer the advantage of a high discharge potential (nearly 4 V) and greater capacities.

Li-Ion Microbatteries



Li-Ion Cell Layout

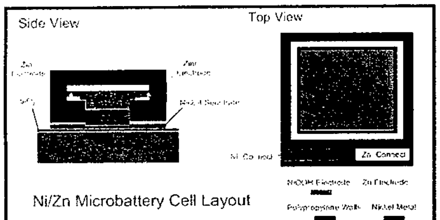


$LiAl_{0.14}Mn_{1.86}O_4$ [2] Composite Microcathode Discharge (vs. Li) at 0.5 mA/cm^2 Cell was 0.09 cm^2

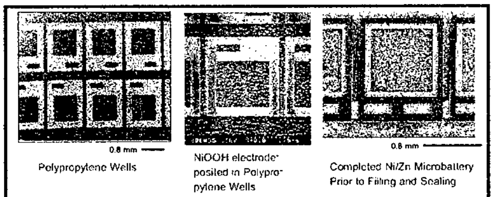
Summary of Li-Ion Microbattery Results

- Anode and cathode microelectrodes fabricated and tested
  - Cathode Capacity > 2 C/cm^2
  - Anode Capacity > 15 C/cm^2
- First generation Li-ion microbatteries fabricated and tested
  - Low cell capacity (<50 mC/cm^2)
  - Limited by masking of the cathode during fabrication
- Second generation Li-Ion Microbatteries under development

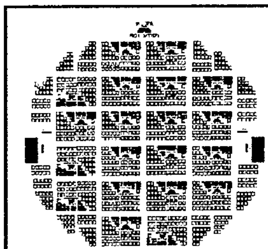
Ni/Zn Microbatteries



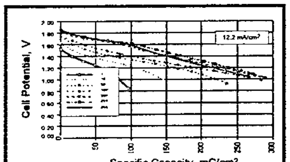
Ni/Zn Microbattery Cell Layout



Micrographs of Ni/Zn Microbatteries at VariousFabrication Stages

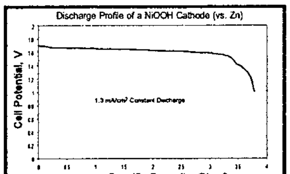


Ni/Zn Battery Layout on a 4 inch Wafer

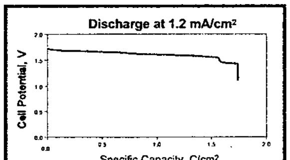


Ni/Zn Microbattery Cycle Data

A parallel array of 6 cells 0.0009 cm^2 each



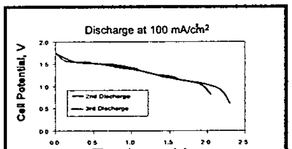
Discharge Profile of a NiOOH Cathode (vs. Zn)



Ni/Zn Microbattery Discharge Profile

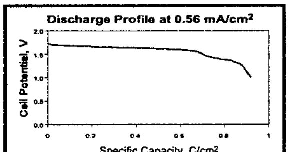
A parallel array of 2 cells 0.008 cm^2 each

Picture of a Silicon Wafer with Approximately 1200 Microcells



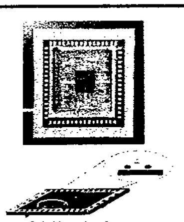
High Rate Discharge of a Ni/Zn Cell

Approximately 1/2 the Capacity was accessed

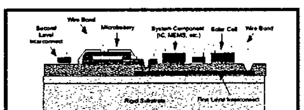


Sealed Ni/Zn Microbattery Discharge

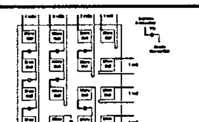
Microbattery Integration



Flip Chip Integration of MUMPS and Electronics at MCNC [3]



Power Source Integration



Microbattery Arrays

Results and Conclusions

- Li-ion Microelectrodes have been fabricated and tested
- Fabrication and testing of initial Li-ion Microbatteries complete and improved design in progress
- Ni/Zn Microbatteries have been discharged at rates up to 100 mA/cm^2 (150 mW/cm^2)
- Specific capacity of the NiOOH cathode: >2 C/cm^2
- Ni/Zn Microbatteries were cycled over 250 times to 100 % DOD
- Performance of Ni/Zn Microbatteries (capacity and power) suitable for use with MEMS devices.
- Significantly greater capacities anticipated from Li-ion Microbatteries

This work was sponsored by the Ballistic Missile Defense Organization (Contracts F33615-96-C-2674 and F33615-97-C-2785) and the U.S. Air Force (Contract F29601-96-C-0078). Their support is gratefully acknowledged.

References:
1. Puers, R. and P. Wouters, "Adaptable Interface for Flexible Monitoring of Temperature and Movement." Analog Integrated Circuits and Signal Processing 14 (3) pp. 193 206 (1997)
2. Doddapaneni, N. and D. Ingersoll, US Patent 5,567,401 (1996)
3. MCNC, "MCNC MEMS Technology Applications Center", http://MEMS.MCNC.org/. (1998)
4. L.G. Salmon is currently at CWRU.

A Microfluidic Sample Preconditioning System for CBW Agent Detection and Quantification

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Department of Bioengineering, University of Washington, Seattle WA, 98195, USA.

Fundamentals of Microfluidics

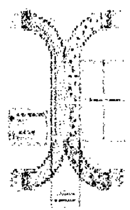
The Reynolds number (Re) is ratio of inertial forces to viscous forces in a fluid system,

$$Re = \frac{\rho v l}{\eta}$$

where ρ is fluid density, v is fluid velocity, l is a characteristic length dimension, and η is fluid viscosity.

In microfluidic channels, Re is generally much less than 1. Low Reynold's number flows exhibit transport by diffusion and stable laminar flow profiles.

The H-filter

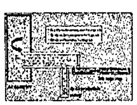


One microfluidic device that utilizes low-Re number phenomena is the H-filter. Small, quickly-diffusing molecules will diffuse rapidly from one input stream to the other while slowly-diffusing particles, such as large proteins or microspheres remain, for the most part, in the input stream.

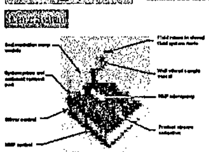
Such a system can be used to perform diffusion-based diagnostics by measuring the extent of a reaction. For example, the concentration of a particular analyte could be detected by monitoring how the color of a pH indicator changes as the target analyte diffuses between streams.

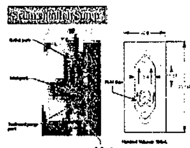
There are a variety of external fields that can be applied in order to induce other types of migration in microfluidics. One possibility is gravity, which can be used to separate particles by specific gravity. Another is the use of an electric field to separate or concentrate particles based on isoelectric point and electrophoretic mobility. Similarly, a magnetic field can manipulate the movement of magnetic particles.

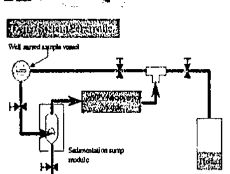
Demonstration System with Sedimentation Sump

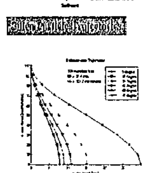


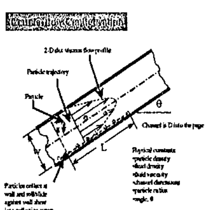
A homogeneous suspension provided by an air-sampler is delivered into the sedimentation stage of the CBW detection unit at a flow rate determined by the micropump. The first stage of the unit is a sedimentation sump, where all rapidly-sedimenting particles are separated from the rest of the sample. A working demonstration of this device has been fabricated. Processing 100 µL of sample per minute, the sump collects 4 µm silica particulate mixed at 0.5% (w) in a buffer solution that also contains 0.025% (w) of polystyrene.

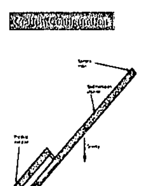




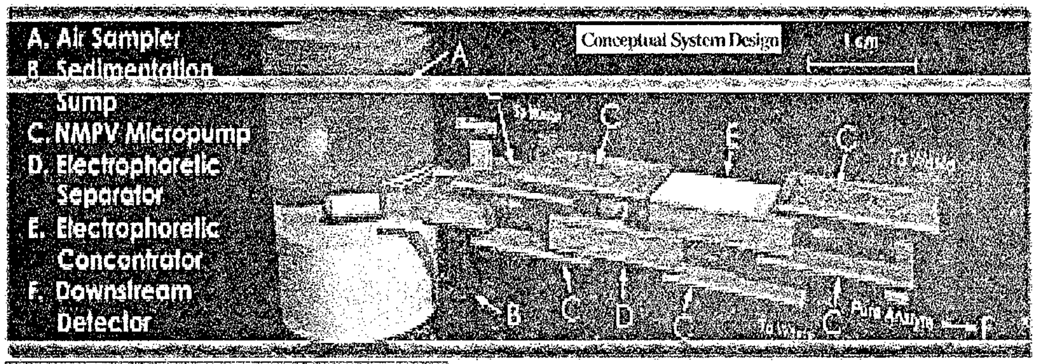








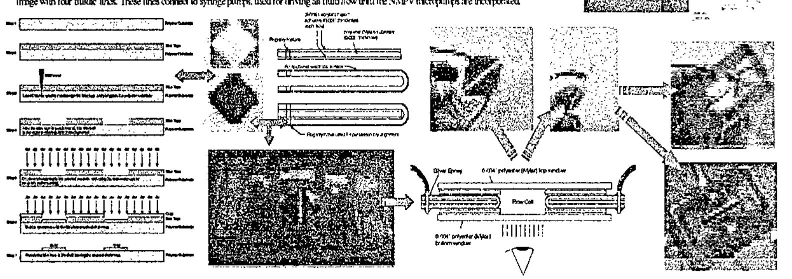
Conceptual System Design



Acknowledgements: This work is supported by DARPA, as part of the Microfluidics program

Electrochemical Flow Cell Design and Fabrication

Electrophoretic flow cell components are fabricated in polymers using laser ablation micromachining methods. Laser micromaching is also used to enable a rapid means of creating a lift-off mask for the patterning of gold electrode. The electrodes are deposited without an intermediate adhesion layer metal. This sputter deposition is made possible by a new combination of techniques involving activation of the mylar surface with an O2 plasma prior to gold deposition. Inividual flow cell components are assembled using a acrylate based pressure sensitive adhesive commonly used in the manufacture of disk drives (3M-1151). Components are positioned relative to each other to form a precise channel geometry using a variable assembly jig. Different aspect ratios can be attained by using different electrode thicknesses by adjusting (with registry features in the electrode and assembly jig) the gap spacing during assembly. Non-compliant polymer HPLC tubing is firmly held in alignment by the manifolds with the aid of PDMS gaskets. The fully-assembled unit is shown inverted in the second image with four fluidic lines. These lines connect to syringe pumps, used for driving all fluid flow until the NMPV micropumps are incorporated.



Background: Isoelectric Focusing and Formation of pH Gradient

The majority of research into implementation of electrophoresis in microscale devices has focused on capillary electrophoresis, in which the electric field is applied parallel to the direction of fluid flow and samples are processed in batch mode. However, our group is currently working on implementing zone electrophoresis (ZE) and isoelectric focusing (IEF) in microfluidic devices. In both ZE and IEF, the electric field is applied perpendicular to the direction of fluid flow. This change in geometry allows continuous sample processing while presenting several challenges in device construction.

IEF takes advantage of the amphoteric nature of many biological particles, such as bacteria, by co-localizing a pH gradient and an electric field. If the pH gradient brackets the isoelectric point of a particle, that particle will migrate via electrophoresis to its isoelectric point, at which point it becomes neutrally-charged.

At potentials higher than 1.3V, electrolysis of water will occur in the channel.

Anode, +

$H_2O \Leftrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$
or
$2OH^- \Leftrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

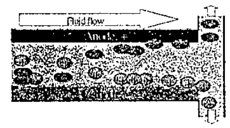
$2H_2O + 2e^- \Leftrightarrow 2OH^- + H_2$
or
$2H^+ + 2e^- \Leftrightarrow H_2$

Cathode, -

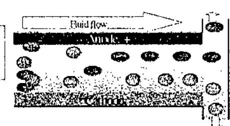
Anode: Oxidation and production of O_2 with either production of H^+ or depletion of OH^-, resulting in net local acid region.

Cathode: Reduction and production of H_2 with either depletion of $H+$ or production of OH^-, resulting in net local alkaline region.

Zone electrophoresis
Strong buffer, uniform pH,
select on electrophoretic mobility

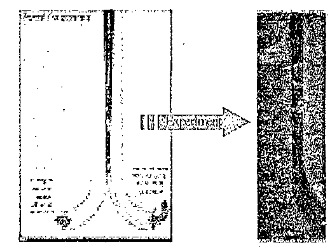


Isoelectric focusing
Weak buffer, pH gradient
formed by electrode reactions,
select on isoelectric point



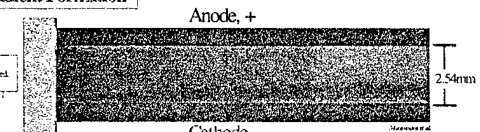
Quantitative Analysis

One method of downstream detection involves imaging the fluorescence signature of a particular molecule. The fluorescence intensity spectrum of experiment can be fit to an analytical model derived from first principles. The unknown model parameters, which include input concentrations, diffusion coefficients, and chemical reaction kinetic rate constants, are adjusted to achieve a best fit. If reaction rate constants are know the model can be used to estimate the concentration of a target molecule. Conversely, the model may be used to estimate reaction rate constants if initial concentrations are known. Thus, the model enables both detector and sensor configurations.

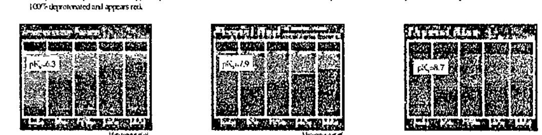


pH Gradient Formation

1mM histidine,
0.2mM phenol red,
starting pH=6.1

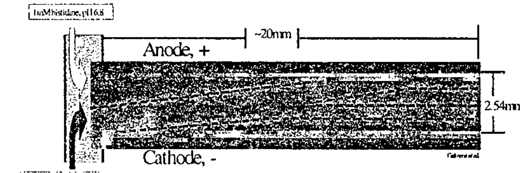


This image shows the development of a pH gradient over time in a static system in a channel of the same dimensions shown above. As before, an electric field was applied (2.3V resulting in a current density of 0.005-0.008mA). Each image is scaled to correspond the length of the channel that would be traveled by a solution flowing at 0.08 µL/s for the duration of the time interval between taking the image and the subsequent image. Phenol red, an absorbing pH-indicator dye with pKa=7.9, was added to the same buffer solution used in the bacterial experiments shown above. At the starting pH of 6.1, the dye is 100% protonated and appears yellow. As an alkaline area forms at the cathode, the pH increases and the dye becomes less protonated until it is 100% deprotonated and appears red.



Preliminary results of bacterial isoelectric focusing

1mM histidine, pH 6.5



1mM histidine with ~1e6 cfu/ml, fluorescently labeled *E. coli*

This image represents five separate images taken during a single experiment after an entire device volume had passed through the device. The intensity variation seen in each image is an artifact of the fluorescent optics used during the experiment. The DNA-intercalating dye Syto 17 (Molecular Probes) was used to stain the *E. coli* λ strain. Images were taken using a 3-chip cooled CCD camera at an exposure of 2 seconds.

The figure above demonstrates the effects of applying an electric field (2.3V resulting in a current of 0.005-0.008mA) to a flowing system containing bacteria in a microelectrofluidic device (gold electrodes on a polymer substrate). The total flow rate in the channel was 0.08 µL/s. Assuming plug flow in the field direction, the average time to travel the distance shown above was 5 minutes. The bacteria, which are negatively-charged, initially migrate to the anode (top of channel). As a pH gradient develops, the bacteria appear to segregate into two populations, one that moves immediately adjacent to the anode while the other migrates to a position that corresponds to a sharp pH gradient (see the figure below). These results indicate the presence of at least two different bacterial populations, each with a different pI. These populations could represent living and dead bacteria, or normal variation within a single bacterial strain.

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MEMS/VLSI Electrochemical Sensing for Chem/Bio/Neuro

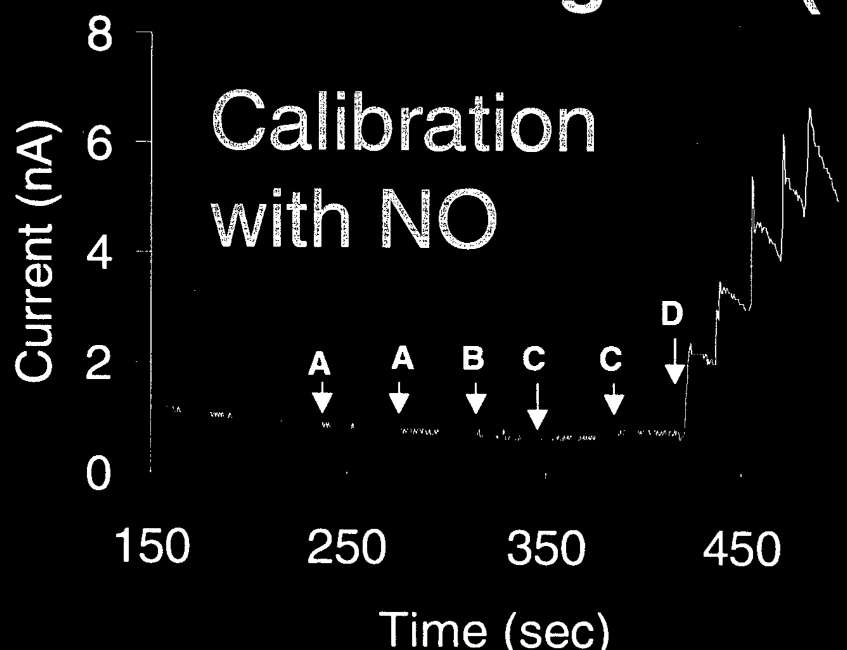
Nitish V. Thakor, Raj Rangarajan and Tommy Wong
Johns Hopkins University & ARL
nthakor@bme.jhu.edu
www.bme.jhu.edu/~nthakor

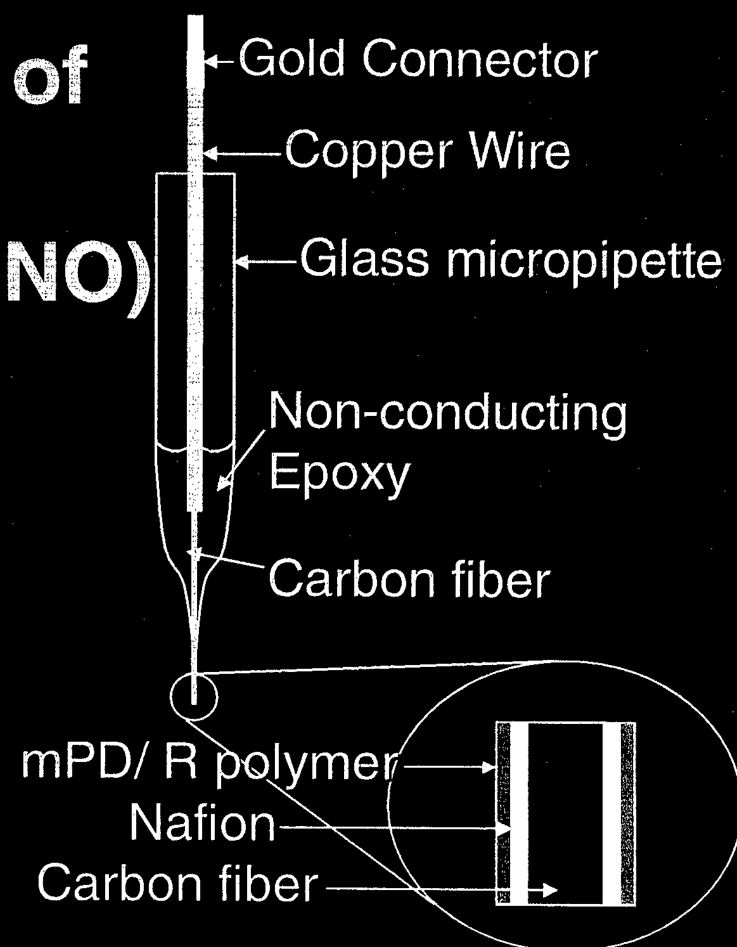
Electrochemical Sensor

Johns Hopkins University

Department of Biomedical Engineering

Suitable for detection of neurotransmitters, chemical agents (e.g. NO)





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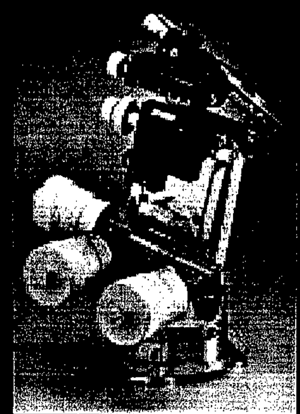
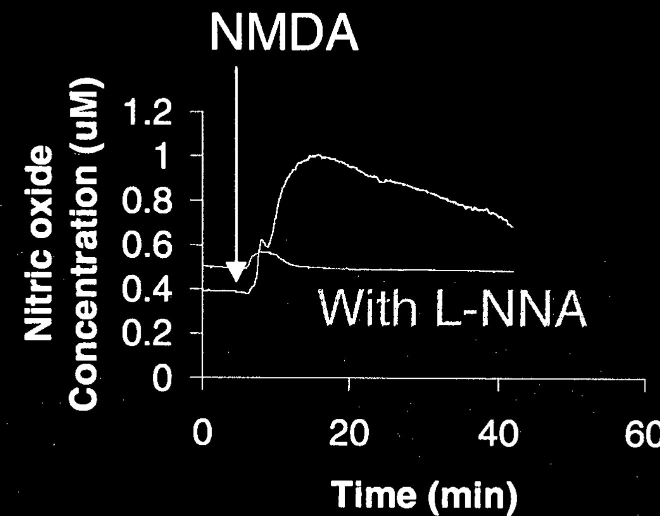
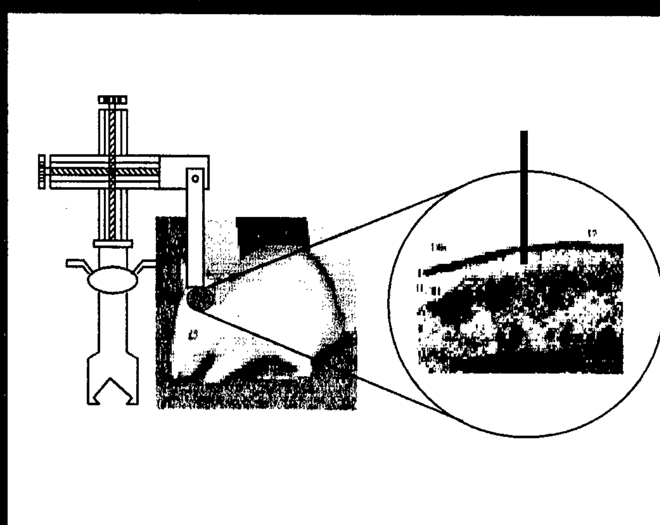
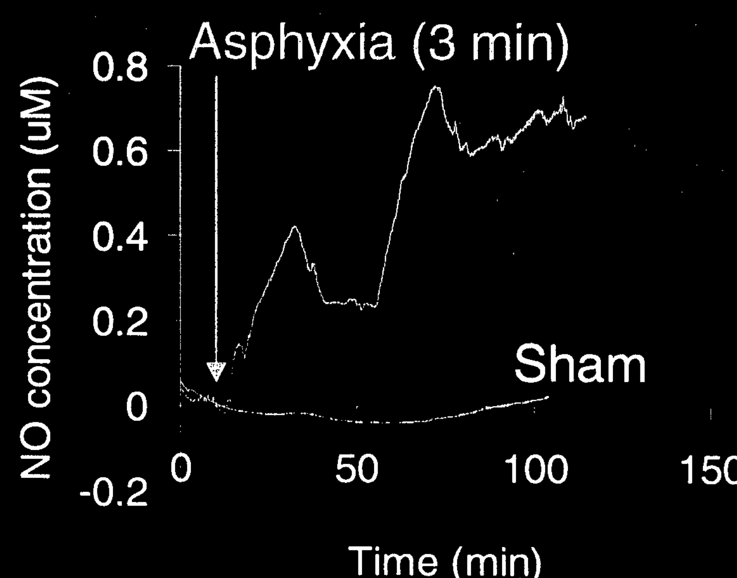
In Vitro and *In Vivo* Experiments









Multichannel Potentiostat

Useful for multichannel measurement of chem/bio sensing

- several neurotransmitters
- merge electrophysiology with electrochemistry
- spatial measurement of a single neurotransmitter
- Other potential applications: optical detection, molecular probe chips

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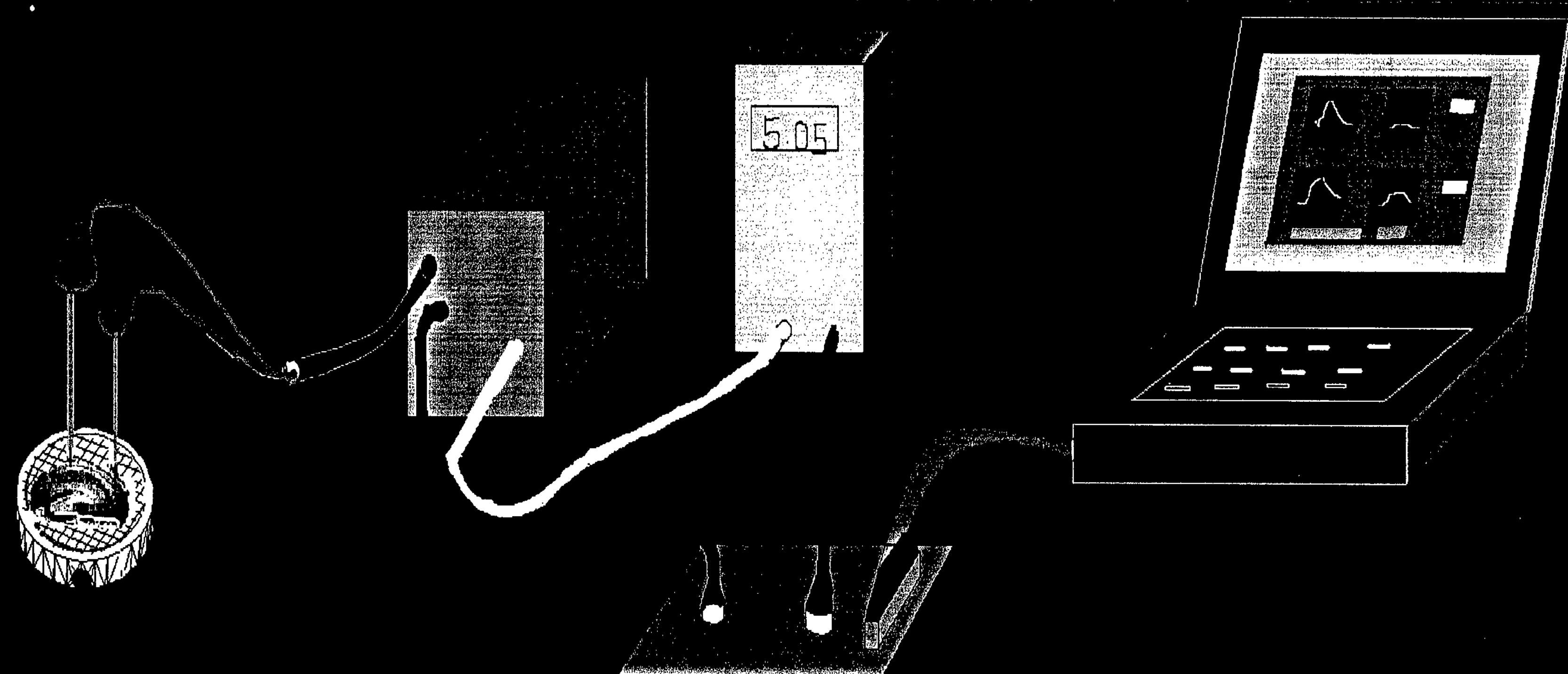
Multichannel Chem/Bio Device from Discrete Sensor and ICs

Johns Hopkins University

Department of Biomedical Engineering

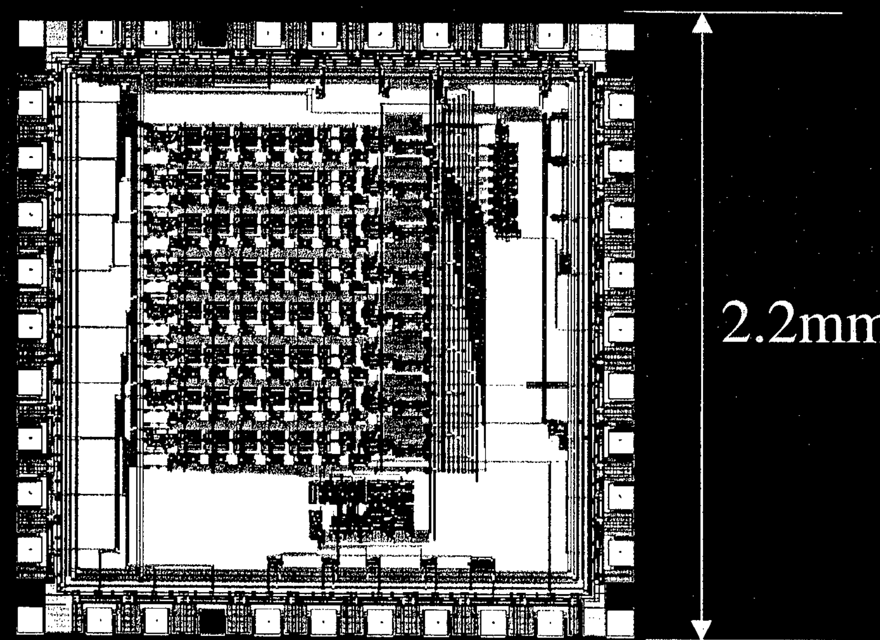


VLSI Multichannel Potentiostat

Johns Hopkins University

Department of Biomedical Engineering

- Smaller in size
- Eight channels in one chip
- Single bit digital output
- Integrated with μsensor using MEMS technology



Multichannel potentiostat chip

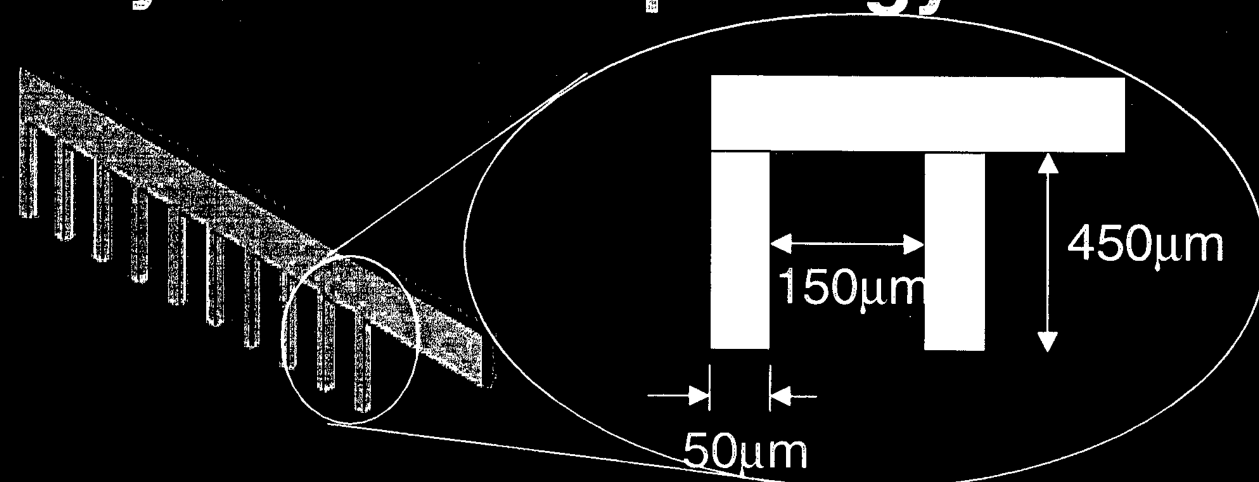
Multichannel Chem/Bio Sensor Array

Johns Hopkins University
Department of Biomedical Engineering

- Integrate Microsensor with VLSI
- Carbon MEMS technology
  - Carbon gives improved electrochemical detection and biocompatibility as to electrophysiology/electrochemistry
- Advantages of microfabrication
  - small size, low cost
  - controlled process
  - mass production, disposable

Carbon Microstructures

- Useful for multineurotransmitter arrays
- Free standing microstructures
  - Provided by Dr. George Whitesides, Dept. of Chemistry and Chemical Biology, Harvard University
- Glassy carbon morphology



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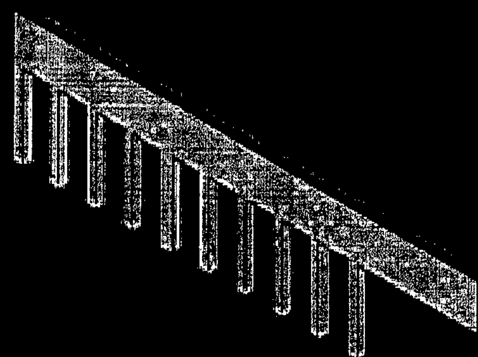
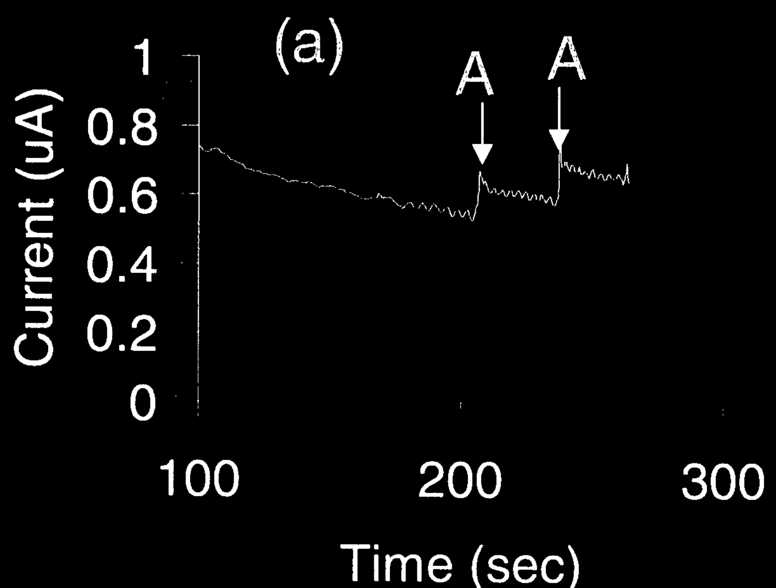
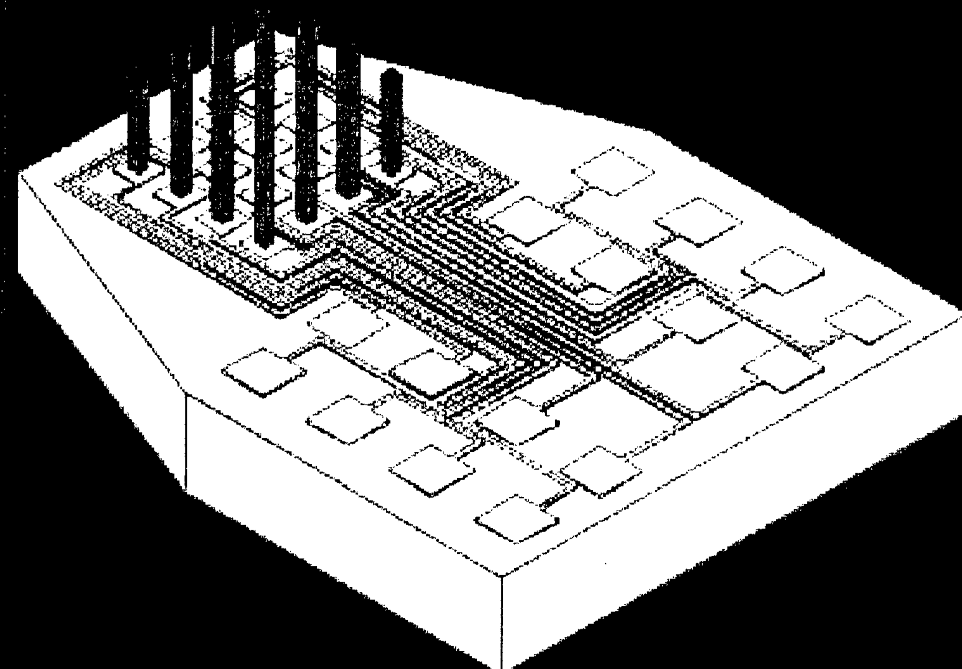
Carbon Multielectrode Array

Johns Hopkins University

Department of Biomedical Engineering







A "bed of nails" integrated sensor array made from carbon microstructures

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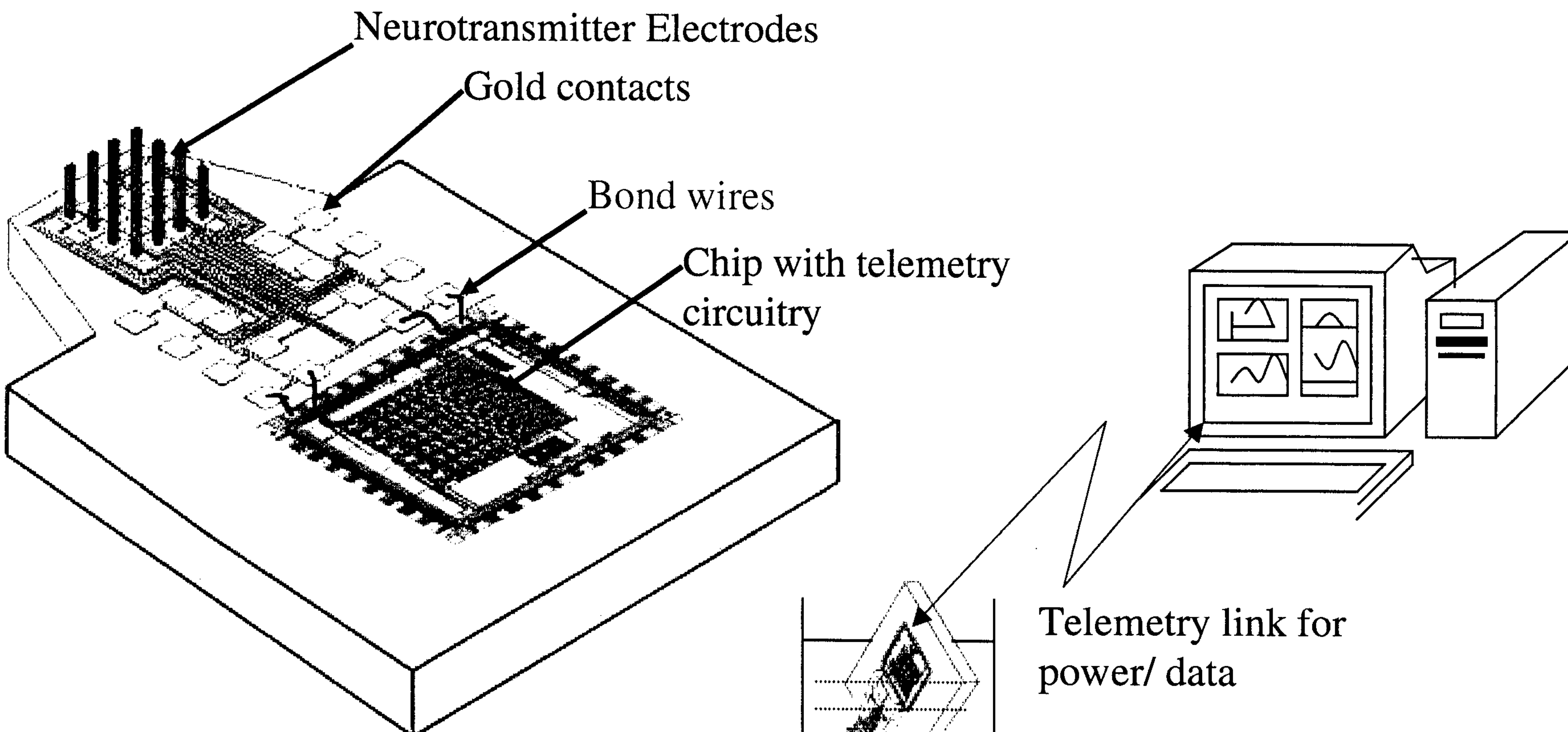
Integrated Sensor Array

Johns Hopkins University
Department of Biomedical Engineering

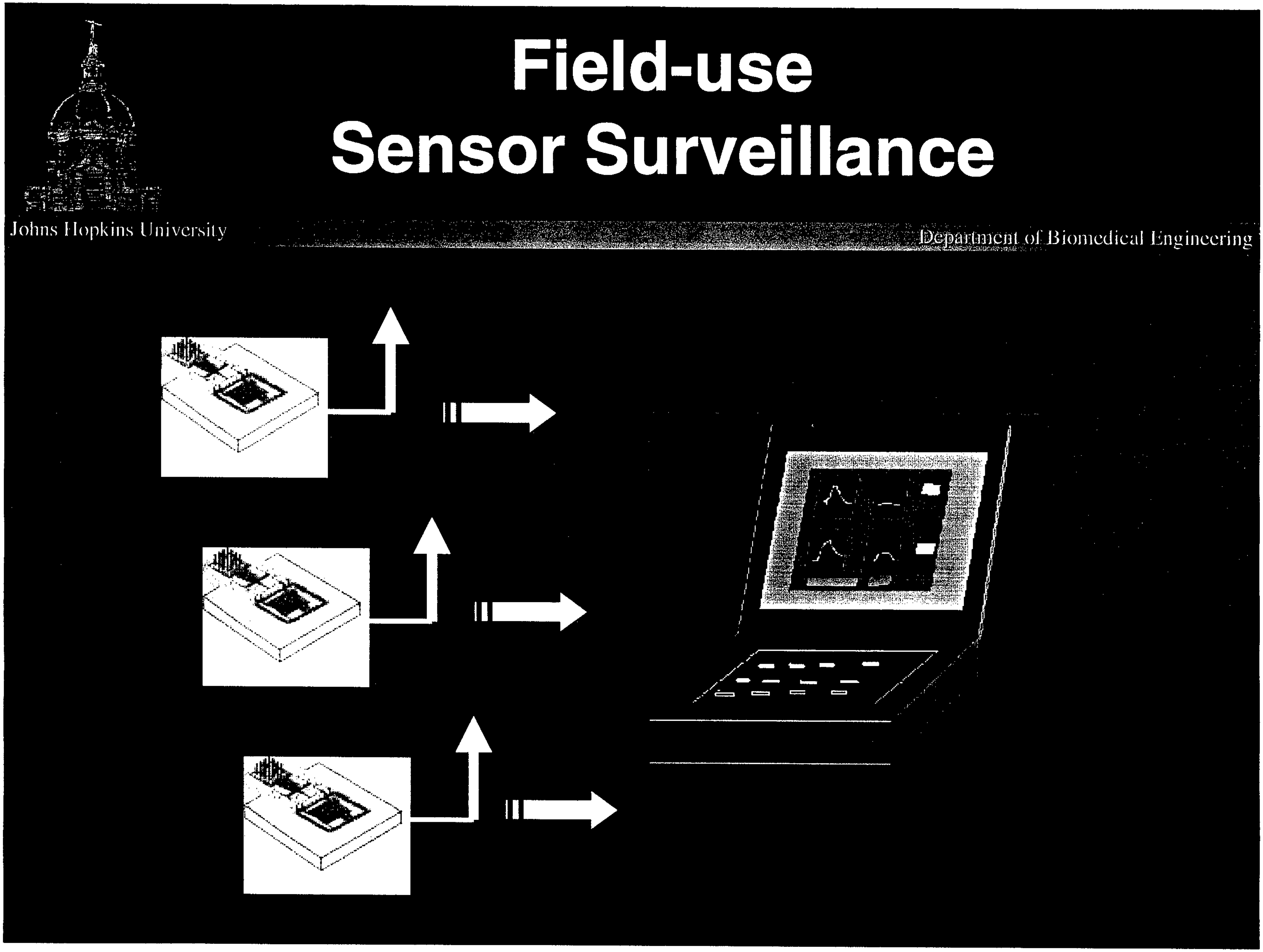
- Carbon MEMS sensor
- VLSI potentiostat
- Integrate both to form a single unit
  - flip chip
  - solder bump
- Incorporate telemetry
  - useful for *in vivo* recordings
  - useful as a dispersible sensor for chem/bio detection in the field

Remote Controlled Sensor Array



Only four bonds shown for clarity

Inductor coil not shown for clarity


Field-use
Sensor Surveillance
Johns Hopkins University
Department of Biomedical Engineering

Process Intensification Needs in the Refining and Petrochemical Industry

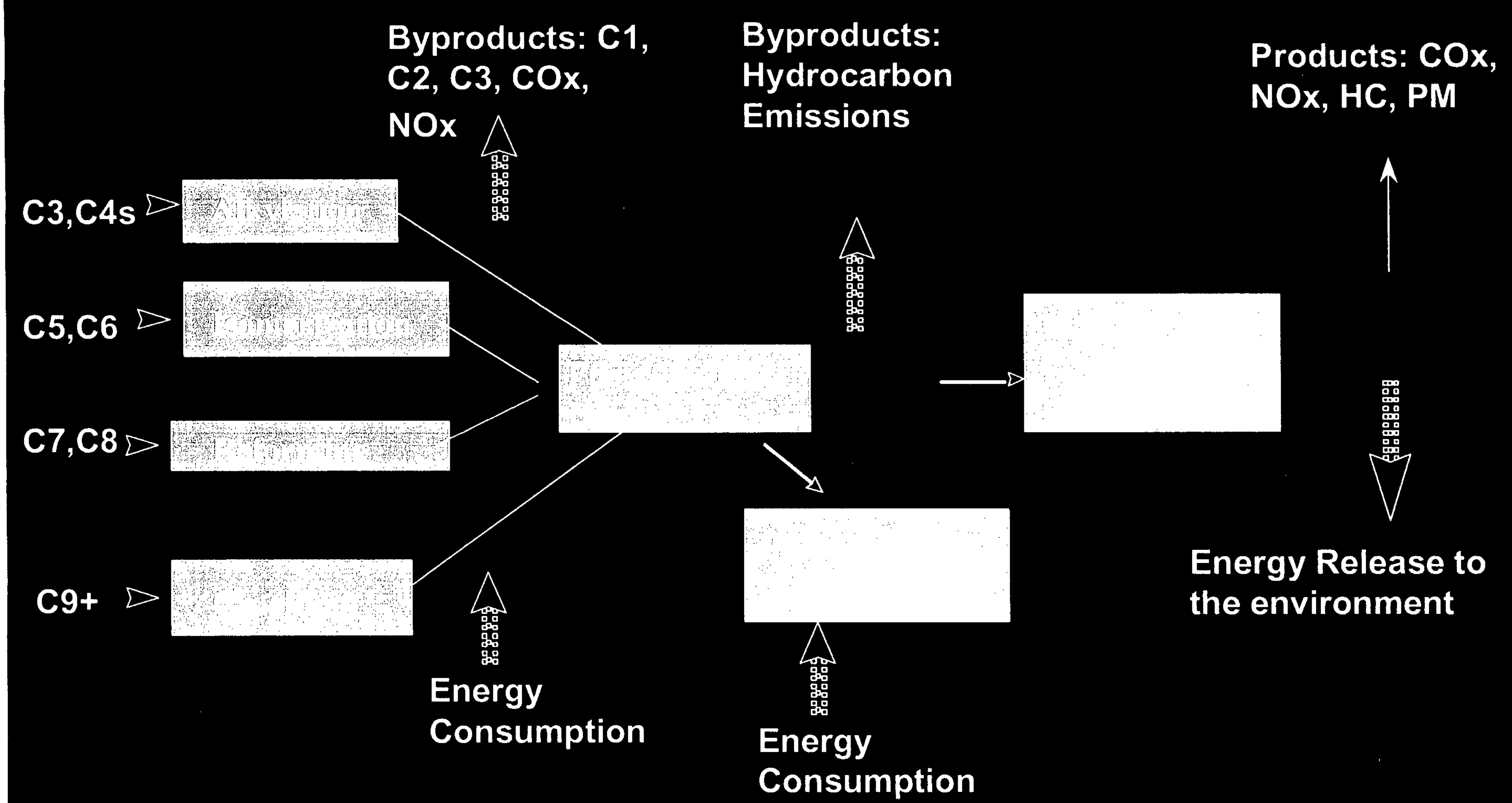
Anil R. Oroskar, Jennifer S. Holmgren and Kurt M. Vanden Bussche

UOP LLC

Research and Development

Des Plaines, IL

Existing Picture of Fuels : Production, Transportation and Use



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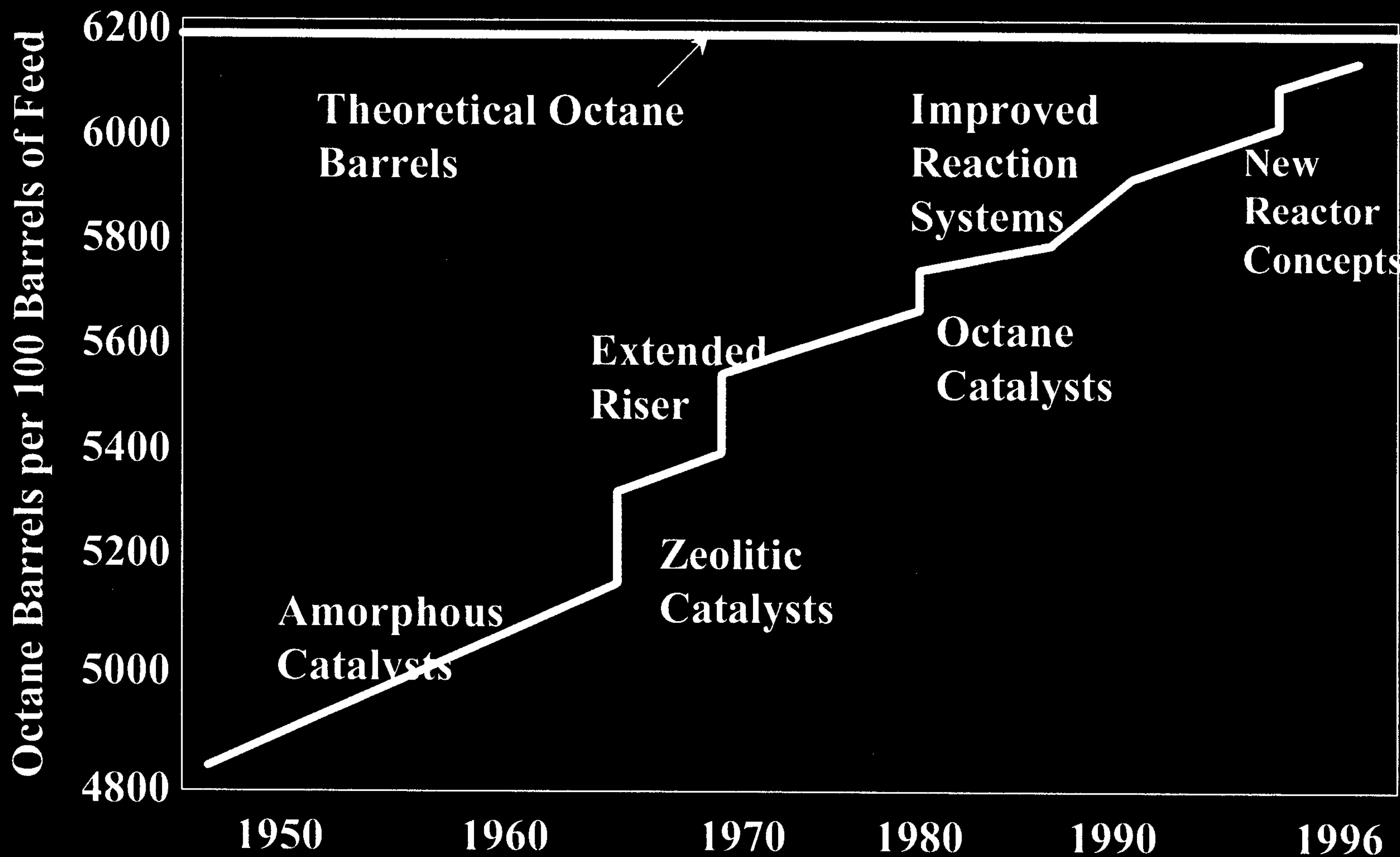
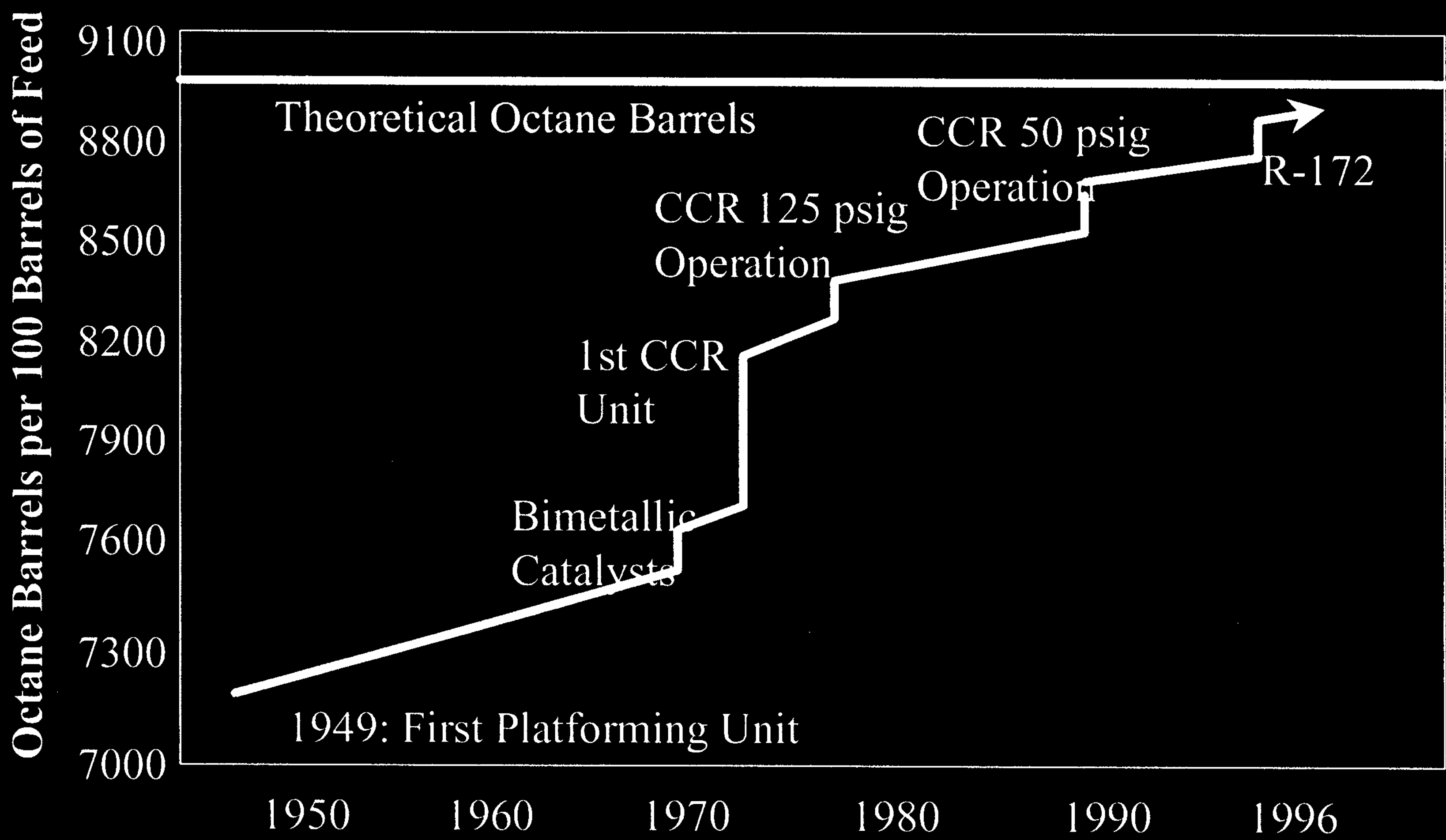
Fluidized Catalytic Cracking: main process to produce gasoline from heavier hydrocarbons, is rapidly approaching its theoretical limits.



Catalytic Reforming: main process to improve the octane number of naphtha, is rapidly approaching its theoretical limit.



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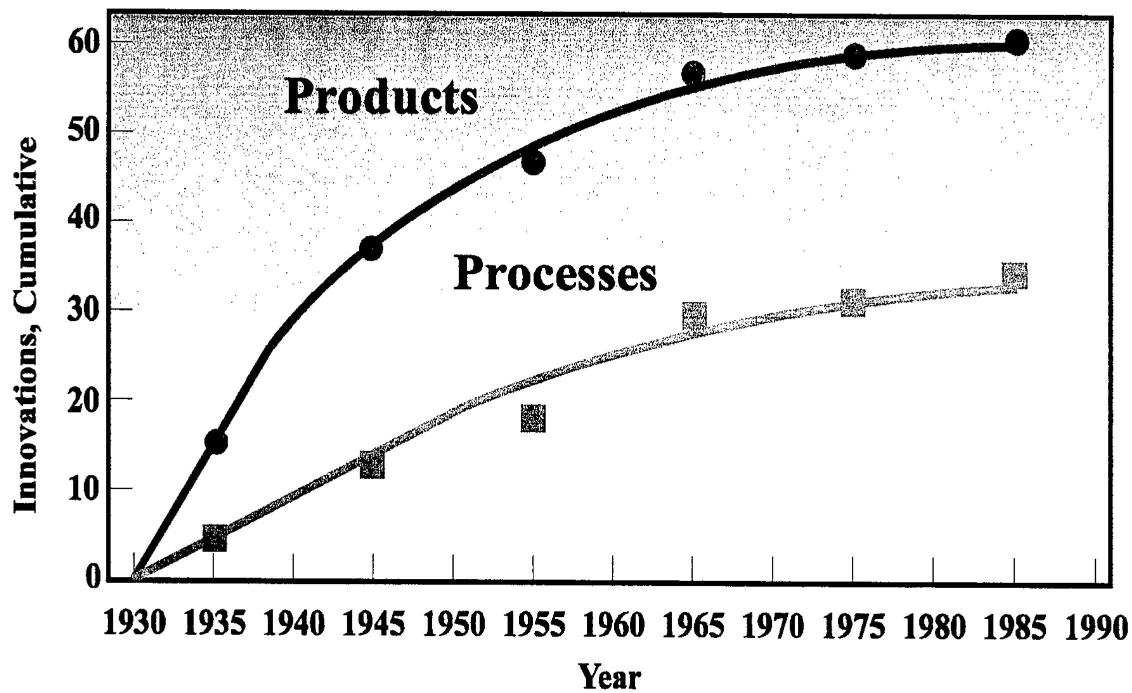
This trend, observed in the conversion and upgrading of processes in refineries, is present throughout the refining and (petro-) chemical industry.

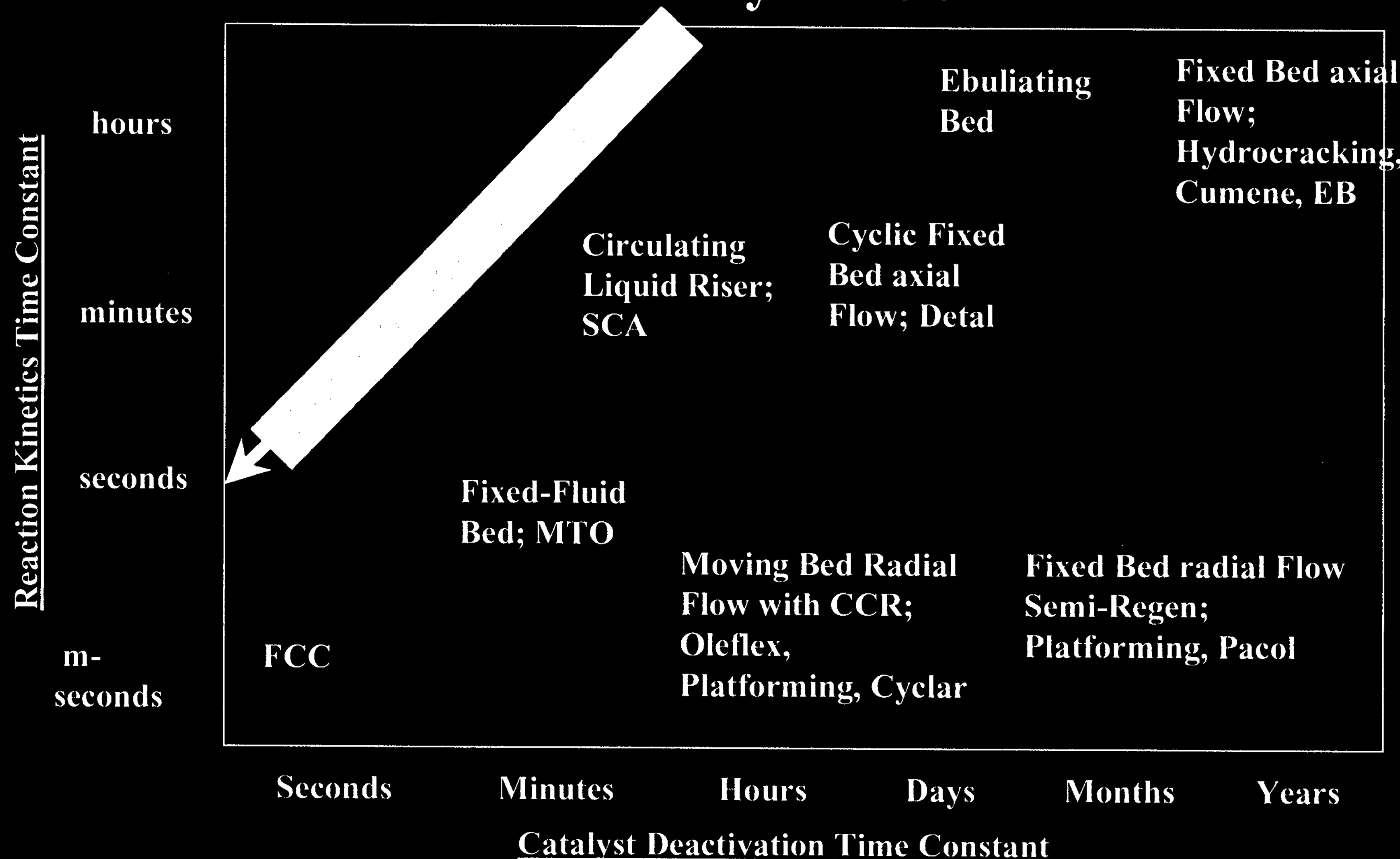


Product and Process Innovations from 1930 to 1985 Are Shown

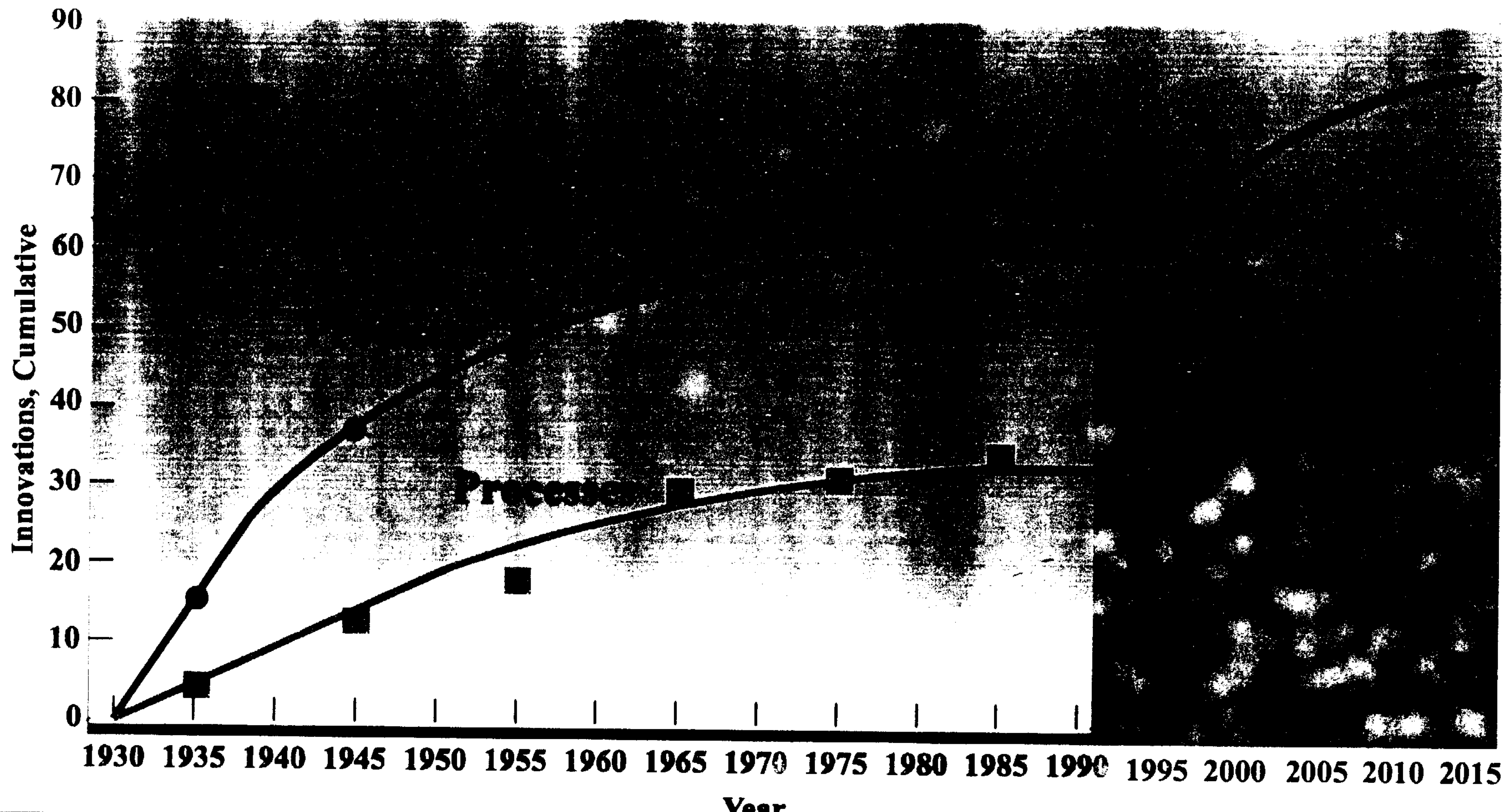
How Process Intensification and Miniaturization Can Play a Role in the Refining and Petrochemical Industry: Drivers and Examples of Key Challenges.

Driver	Problem/Challenge
1. Lower Cost Routes…	Methane, LPG Utilizati
2. Environmental Compatibility…	Liquid Alkylation
3. Improved Product Quality…	Reduce Side Reactions
4. Enable New Synthesis Routes (Chemistry)…	Superior control of Conditions
5. Enable New Process Concepts (Engineering)…	Superior control of heat and mass transfer.

The trend in UOP's Reactor Technology is toward faster and smaller: (micro-)second applications... enter the miniature systems ?



Can miniaturization be an enabler to revitalize the innovation process in the refining and (petro-) chemical industry ?



Novel Microfabricated Pd-Au/SiO_2 Model Catalysts for the Hydrogenation of 1,3-Butadiene

A. C. Krauth and E. E. Wolf

Department of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556

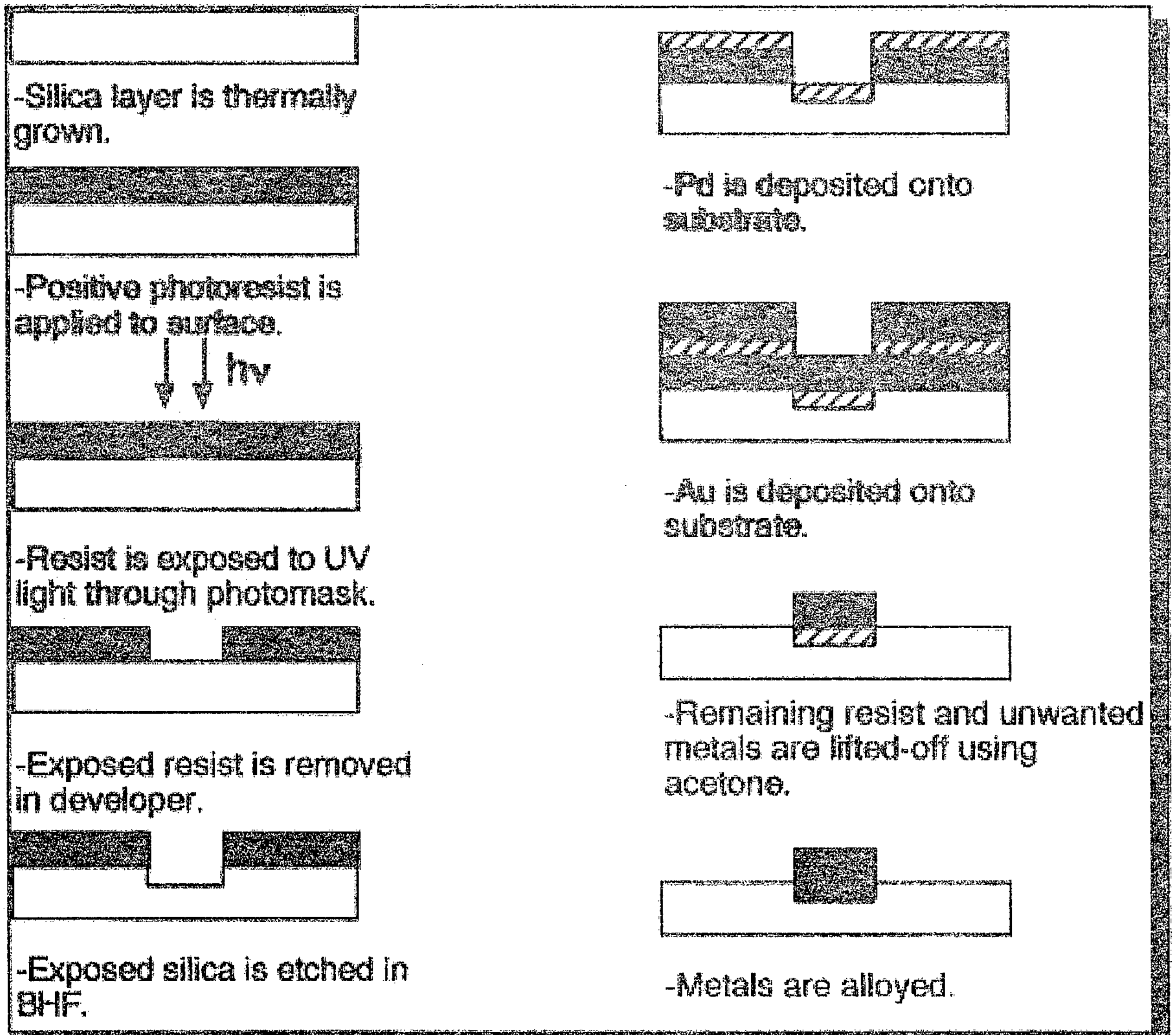
Objectives

- Explore the possibility of preparing a microfabricated catalyst with a controlled and uniform particle composition and study the effect of the particle composition on a model reaction.
- Demonstrate the advantages of the microfabricated catalyst over traditionally prepared supported catalysts.
- To use atomic force microscopy (AFM) to relate the surface morphology to the catalytic activity and kinetic parameters.

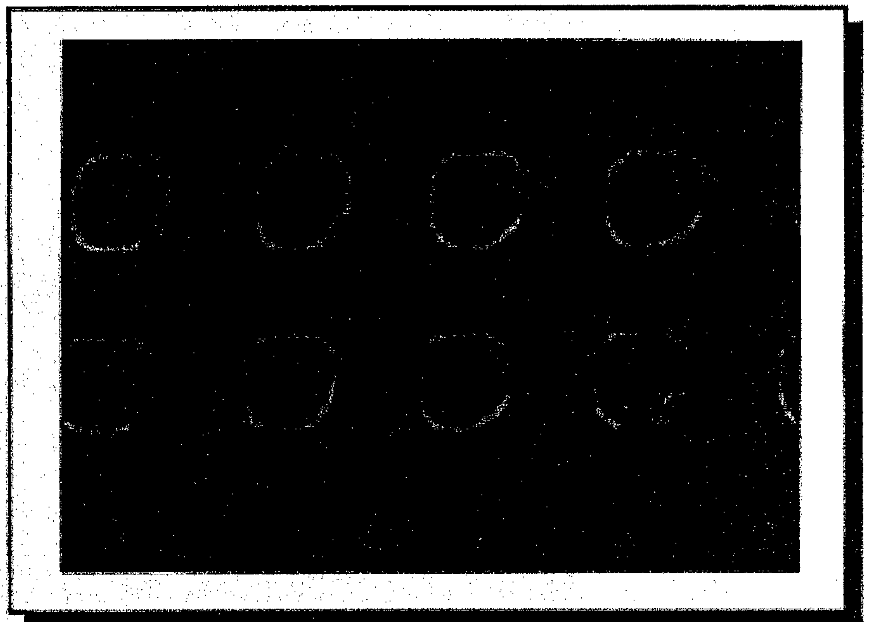
Microfabricated Catalyst vs. Conventional Catalyst

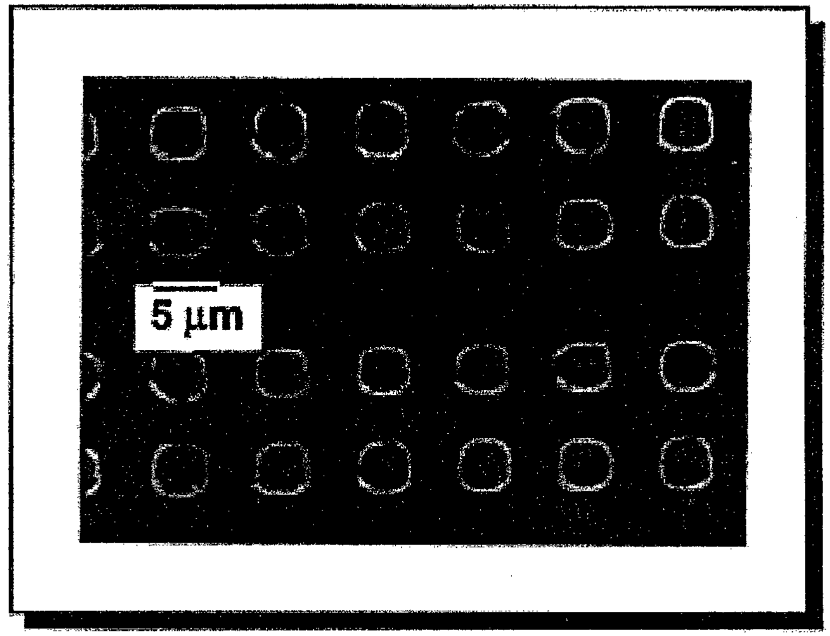
- Conventional Bimetallic Catalyst
  - No guarantee of alloying
  - Particle composition distribution
  - Data represents a statistical average of the entire sample and reflects the preparation method more than the metals used
- Microfabricated Bimetallic Catalyst
  - Preparation procedure guarantees alloying in the absence of phase formation
  - Uniform particle composition
  - Data reflects both the performance of a single particle, as well as the overall catalyst
  - Optimization of catalyst possible, since each particle can be optimized.

Preparation of Microfabricated Catalyst



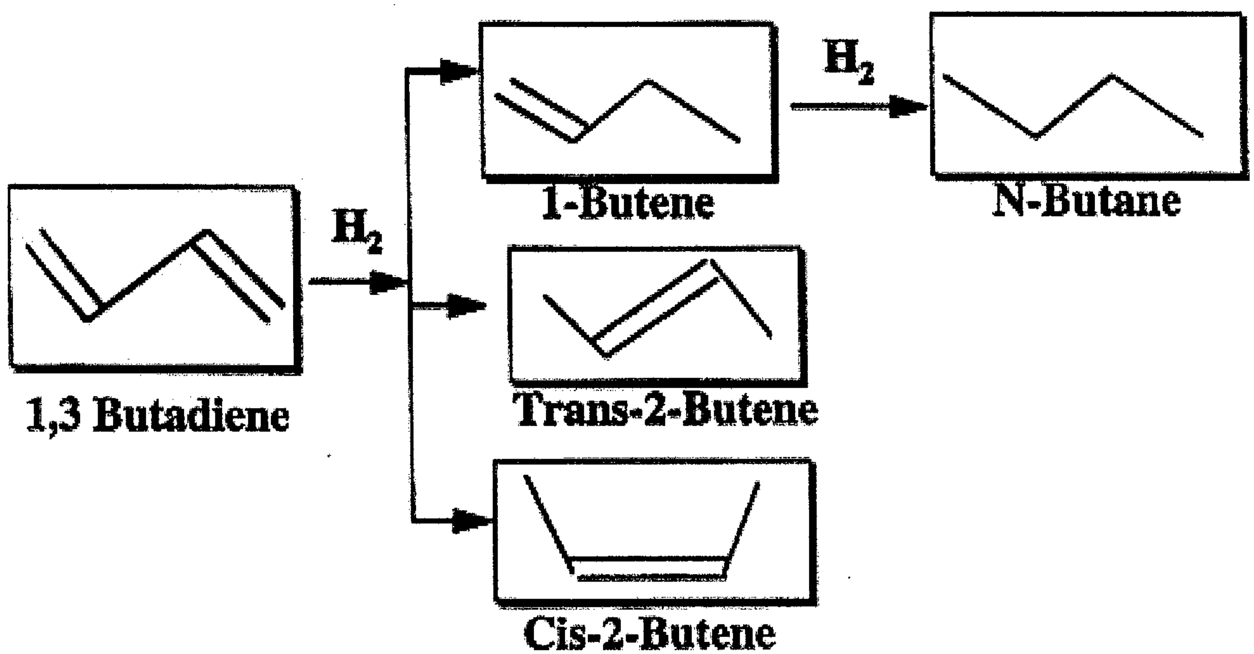
SEM Micrographs of Microfabricated Catalyst





- 4 µm "islands" separated by 4µm spaces
- Probe reaction chosen (hydrogenation of 1,3-butadiene) gives reasonable conversions even for low surface area catalysts
- Krauth, A.C., Lee, K.H., Bernstein, G.H., Wolf, E.E., Catalysis Letters 27, 43 (1994).

1,3 Butadiene Hydrogenation Reaction Mechanism



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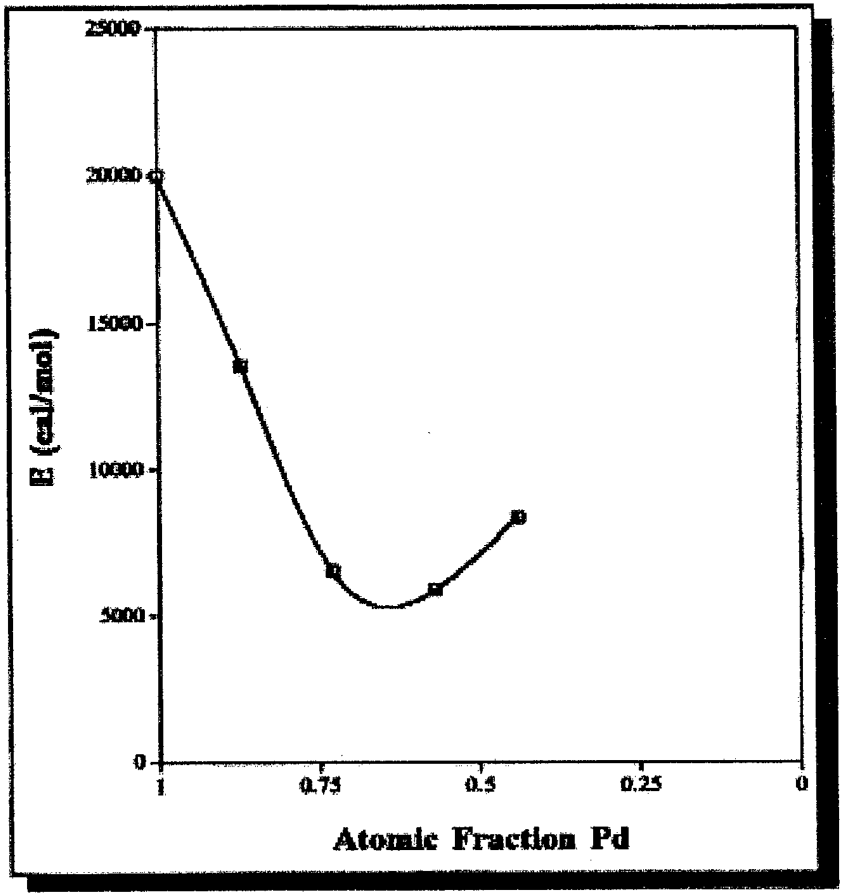
Effect of Composition on Activation Energy



- Minimum corresponds to number of electron holes in the Pd 4d-band (based on bulk composition)
- Suggests that filling of the 4d-band leads to the decrease in activation energy

Summary

- The microfabricated catalyst has the advantage that a true alloy is formed, unlike conventional supported catalysts.
- The addition of Au to a Pd microfabricated catalyst has an electronic effect.
  - Decrease in activation energy
  - Increase in turnover frequency
- The addition of Au to a Pd microfabricated catalyst has a structural effect.
  - Dilution of surface sites
  - Decrease in pre-exponential factor
  - Decrease in conversion
- From the AFM images, parameters such as roughness and average particle size may be important factors in relating the surface morphology to the catalytic activity.
- The presence of Au alters the selectivity of one of the reaction pathways (hydrogenation to 1-butene and further hydrogenation to butane), but not the formation of 2-butenes.

Acknowledgments

- Dr. G. H. Bernstein
- NSF (NSF CTS 92-15339 and NSF ECS 92-53580-002)
- GAANN Program through Notre Dame's Center for Bioengineering and Pollution Control
- NNF at Cornell

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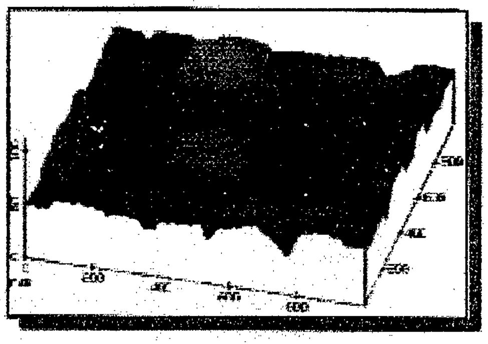
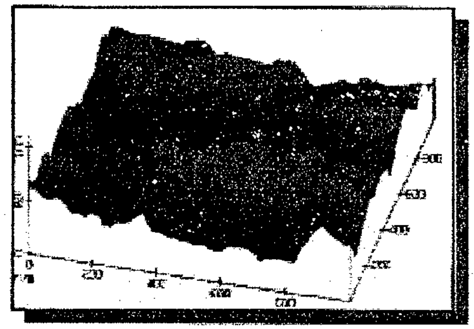
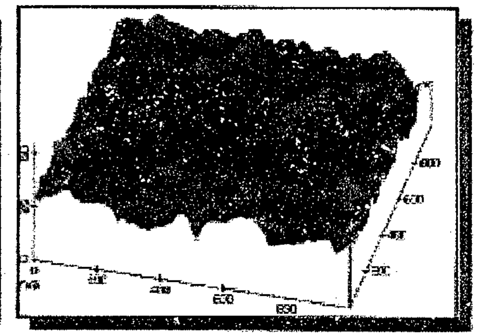
AFM Micrographs



100 at% Pd



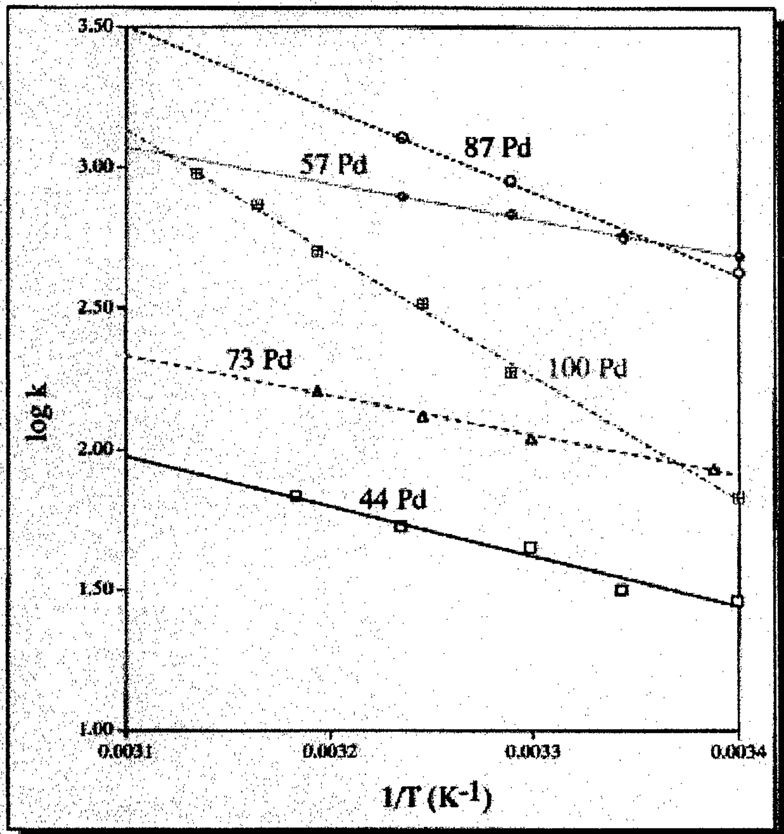
73 at% Pd



87 at% Pd

- Many grains within each "island" (demonstrates need to reduce particle size)
- Pure Pd catalyst has the highest surface roughness
- 73 at% Pd catalyst has the largest particle size
- Remaining catalysts have similar surface structures and parameters

Arrhenius Plot



- Pure Pd catalyst has the largest E_a, pre-exponential factor and smallest rate constant at room temperature
- 57 at% Pd catalyst has the largest rate and smallest E_a at room temperature
- 73 at% Pd catalyst has the smallest pre-exponential factor

A Microscale Chemical Reactor System for Catalytic Dechlorination of Chlorinated Solvents

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Gleeson Hall, Corvallis, OR. 97331

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ABSTRACT

Three types of microscale (electro)-chemical reactors are constructed and tested for their performance in dechlorination of p-chlorophenol.

Micro-Channel Reactor (**MCR**) with Fe/Pd catalyst deposited on the reactor walls, Micro-Bead Reactor (**MBR**) containing polymer micro-beads or polymer layers with nanosize Fe/Pd catalyst, and Micro Electro-chemical Reactor (**MER**)

Conceptual schematic of these three reactor configurations are shown in Figure 1.

JUSTIFICATION

Chlorinated hydrocarbons and particularly chlorinated aromatic hydrocarbons such as PCB's still represent substantial danger during transportation, processing, and destruction. Most commonly used technologies for the separation and destruction of non-chlorinated hydrocarbons in environmental clean-ups, stock elimination, and mixed waste treatment are considered ineffective or are prohibited by federal and state regulations. A catalyst based (electro)-chemical processes for dechlorination of chlorinated aromatics show great potential in solving the most difficult cases of selective treatment of chlorinated hydrocarbons in mixed wastes.

THEORY OF OPERATION

The investigation into the chemical reactions involved in the dechlorination of chlorinated aromatics has produced three separate factors contributing to the overall rate of dechlorination. These include the various (a) dissociation reactions, (b) hydrogen production and (c) removal reactions, and the actual chlorine removal step.

(a) The dissociation reactions involved include the dissolution of iron from the zero-valent state (1), water dissociation (reaction 2), and acid dissociation (reaction 3).

(b) The presence of the hydrogen ion in the reaction system, H+, is controlled by its formation from the dissociation reactions (2, 3), its removal by Fe (reaction 4) or Pd (reaction 5) to form either $H_2(g)$ or the intermediate reactive hydrogen, H*, or recombination to form hydrogen gas bubbles on the catalyst surface (reaction 6). The electrons produced in the iron dissolution reaction (reaction 1) are utilized by the palladium surface to form the highly reactive intermediate H* (reaction 5), which is used in the

(c) dechlorination reaction (reaction 7). Coupling these steps gives the overall dechlorination reaction (reaction 8).

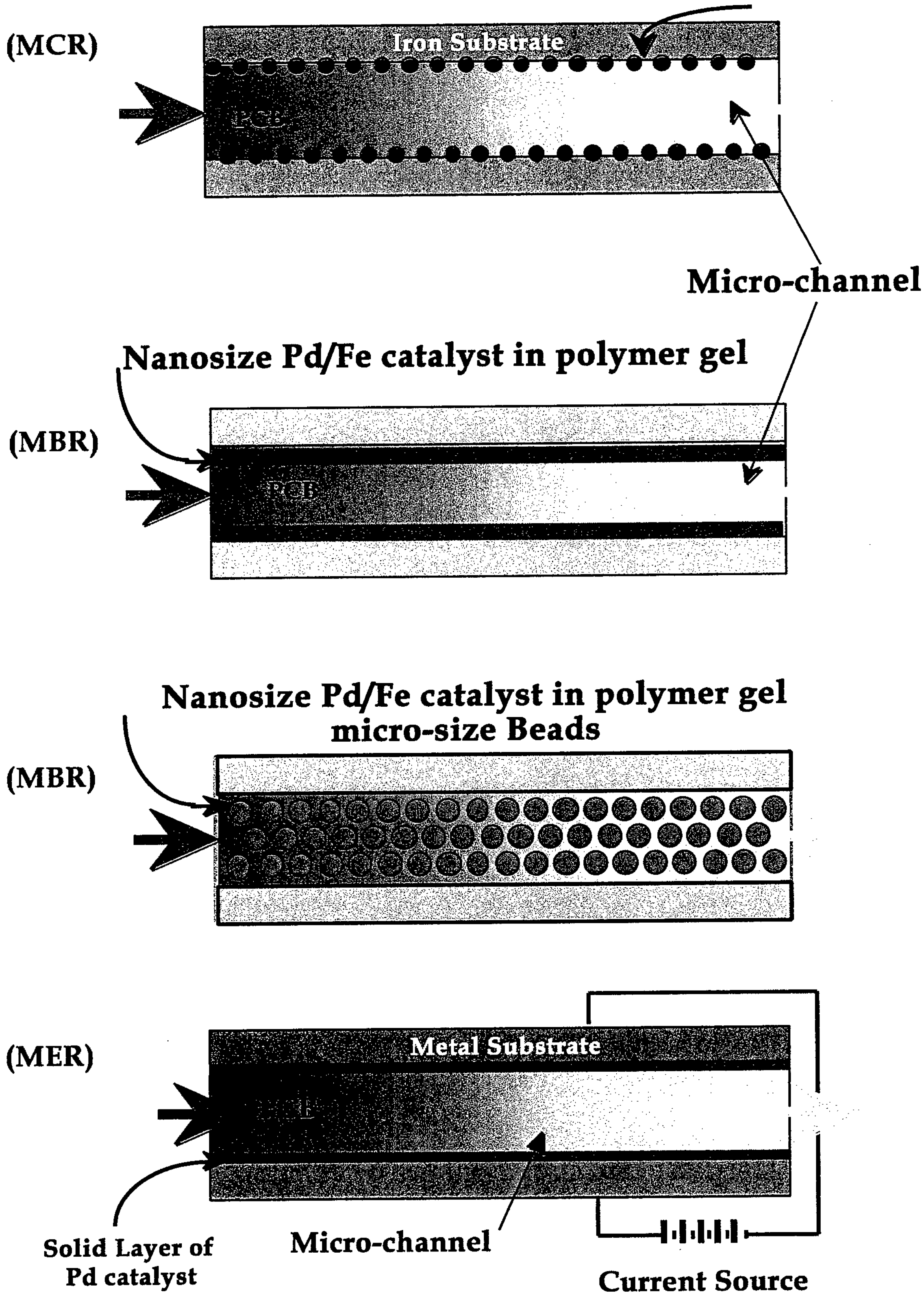


Figure 1.: Three conceptual reactor configurations for dechlorination of chlorinated hydrocarbons.

Dissociation Reactions:

$$Fe^{o} \rightarrow Fe2+ + 2e- \tag{1}$$

$$2H_2O \leftrightarrow 2H^{+} + 2OH^{-} \tag{2}$$

$$2HCl \leftrightarrow 2H^{+} + 2Cl^{-} \tag{3}$$

Hydrogen Reactions:

$$2H^{+} + 2e- \rightarrow H_2\,(g) \tag{4}$$

$$2H^{+} + 2e- \rightarrow 2H^{*} \tag{5}$$

$$2H^{*} \rightarrow H_2\,(g) \tag{6}$$

Dechlorination Reaction:

$$2H^{*} + R\text{-}Cl \rightarrow R\text{-}H + HCl \tag{7}$$

Overall Reaction:

$$Fe^{o} + R\text{-}Cl + H^{+} \rightarrow R\text{-}H + Fe2+ + Cl- \tag{8}$$

Investigation of the chemistry indicated several important operating parameters. These include the extent of Pd/Fe interfacial area, Pd/Fe weight ratio, ratio of Pd/Fe interfacial area to the amount of chlorine to be removed, system pH, and dissolved O_2. Furthermore, important process resistances dependent on the various process parameters are identified: a) formation of $Fe(OH)_2$ and $Fe(OH)_3$, and b) formation of H_2 gas bubbles. Both formation of iron hydroxide, and hydrogen bubbles deactivate the catalyst surface and thus reduce the overall reaction rate.

The above described dechlorination reaction on the Fe/Pd catalyst is schematically represented in the Figure 2 below.

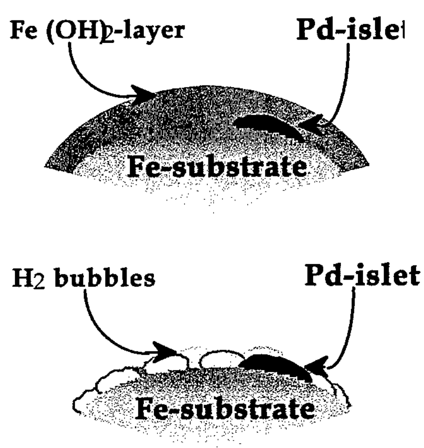


Figure 2.: Formation of iron hydroxide, and hydrogen bubbles deactivate the catalyst surface and thus reduce the overall reaction rate.

Fe/ Pd Catalyst

An electron-scan micrograph of the Fe/Pd catalyst is shown in Figure 3.

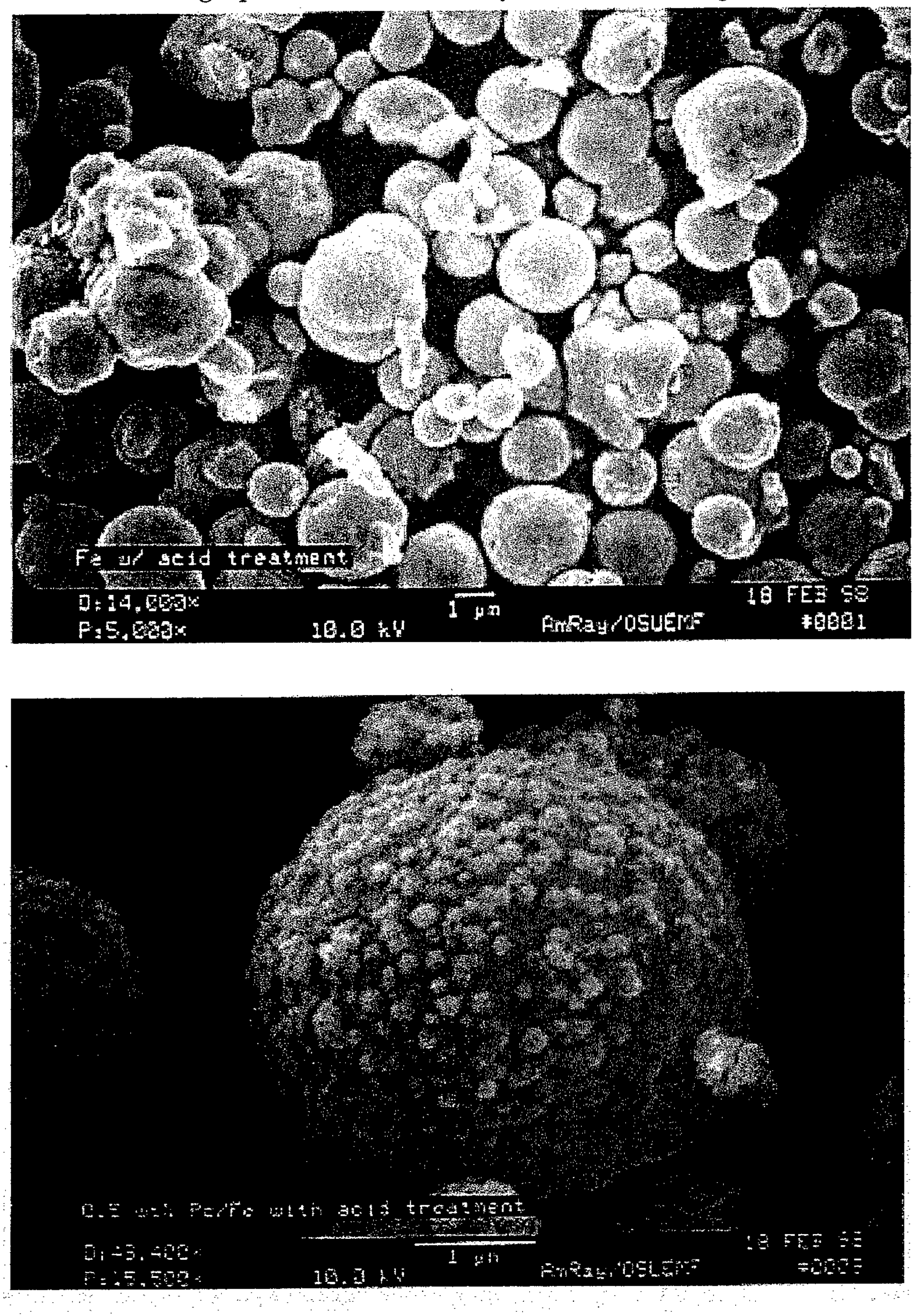


Figure 3.: An electron-scan micrograph of the Fe/Pd catalyst.

EXPERIMENTAL RESULTS

The results of the preliminary testing of the three proposed reactor configurations are shown in the Figure 4 below.

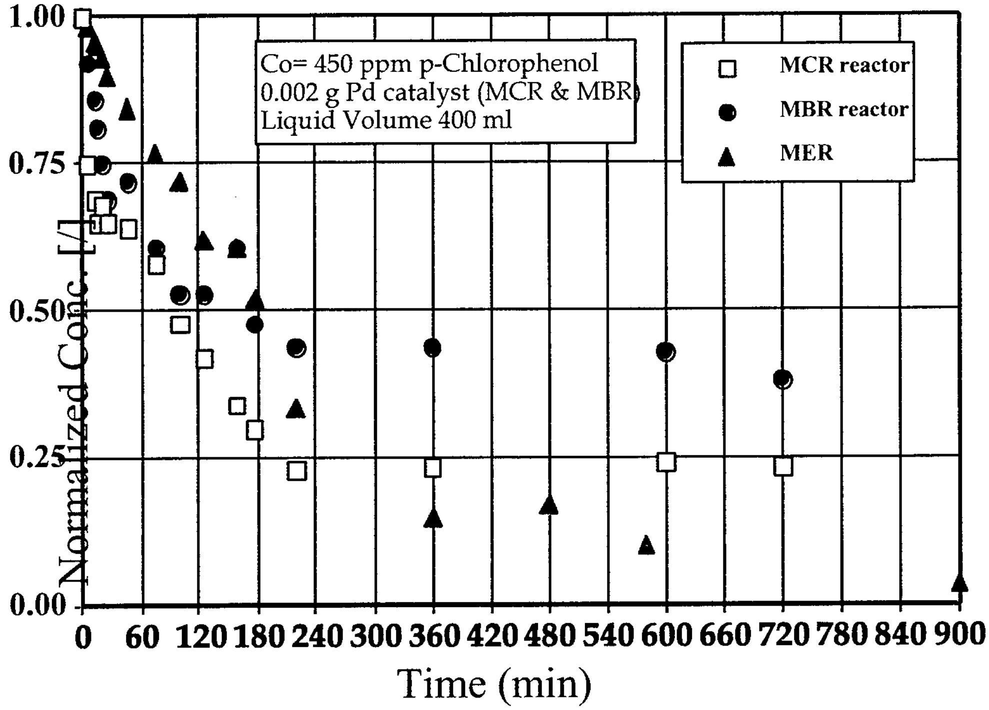


Figure 4.: Experimental results of the three proposed reactor configurations.

MER REACTOR

Our effort to develop a new type of reactor for the dechlorination of chlorinated aromatics is motivated by a possibility to improve the chemical reaction scheme and remove or suppress the above mentioned process resistances.

Reaction (1) indicates that Fe^{o} is sacrificial element in the dechlorination process. The electrons needed for the production of active hydrogen H* by Pd may be obtained from a battery source, thus eliminating the need for the iron substrate and its dissolution into the liquid stream. If Fe^{o} is eliminated from the reaction scheme, the formation of $Fe(OH)_2$ and $Fe(OH)_3$ will also be eliminated. This will, in turn, eliminate the need for a low pH environment and create a possibility to control the production of H* and H_2 (g) by changing current density at the walls of microscale reactor channels.

The construction of the MER represents a collection of parallel microchannels whose walls are covered with a thin Pd layer. The proximity of the walls reduces the diffusion path that each element of the fluid has to make from the bulk of the liquid to the catalyst surface. Furthermore, due to their small size microscale reactors facilitate

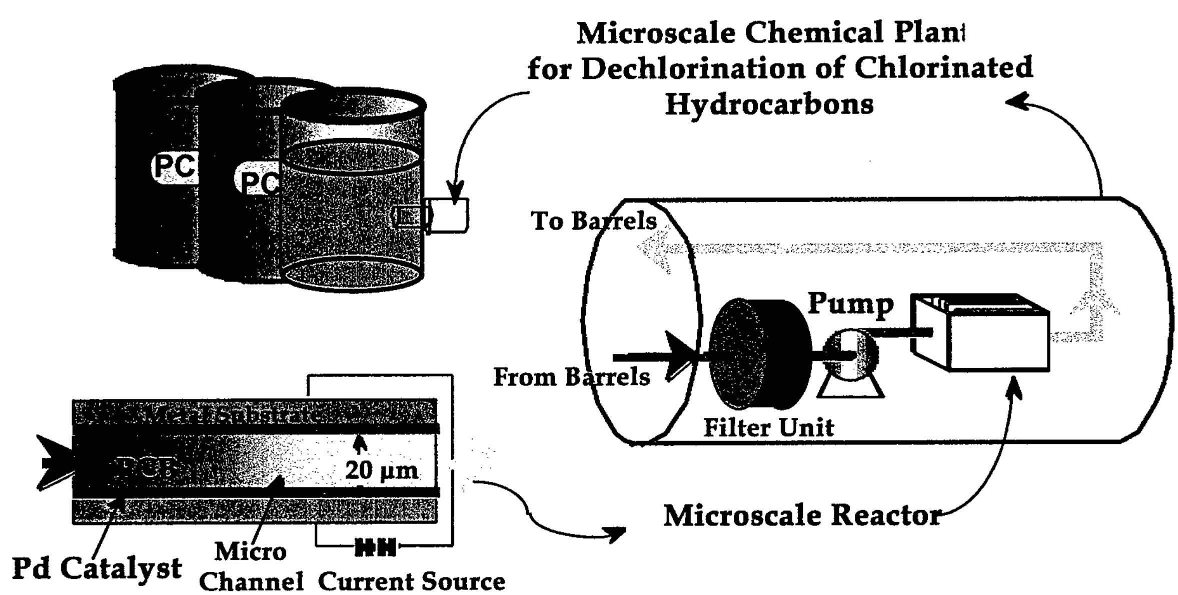
fast response to temperature and concentration changes. The small size makes them deployable in-situ (underground tanks, deep wells) or other hard to reach places.

A microlamination process is used to fabricate the dechlorination reactor. The reactor consists of two sets of four microchannels with each set between two header regions. The reactor array is produced by adhesive bonding alternating laminates of preformed 100µm thick copper shim stock and Kapton KJ polyamide. Microchannel patterned laminates are fabricated from polyamide while microfin-patterned laminates are fabricated from copper. In addition to providing structure, polyamide laminates provide the material for bonding.

Laminates are produced using ESI 8000c Laser Micromachining system with 532 nm Nd:YAG laser. To consolidate the stack, the laminates are registered one to another, compressed and heated within a precision jig. Final bonding conditions are 265 C and 200 kPa for 1 minute. A response surface methodology is carried out on the parameters of time and pressure to minimize fouling of the microchannel while maximizing bond strength.

Coming Soon to Stores Near You

The use of a microscale based system offers the advantage of being able to dechlorinate these products on site, thus minimizing the need for handling and eliminating the need for transportation of these hazardous materials. From a practical standpoint, this imposes a requirement that the reactor and its supporting systems be designed for remote, autonomous operation and that the overall size be such that direct insertion into a 55 gallon drum be easily accomplished.



The prototype system design includes a pump, filter, and the chemical reactor. The entire apparatus is contained in a 50 mm diameter cylinder that is 250 mm long. The maximum flow rate through the system is approximately 0.5 l/min. There are three external connections, a contaminated fluid inlet port, a DC power connection, and a decontaminated fluid outlet port. The apparatus is designed to be operated either in-situ, i.e. submerged in the fluid containing chlorinated hydrocarbons, or externally with connecting lines. Cleanup in a closed container can be accomplished by inserting the device into the container, leaving the inlet and outlet ports open, and connecting to a regulated DC power source.

Liquid-Phase and Multi-Phase Microreactors for Chemical Synthesis

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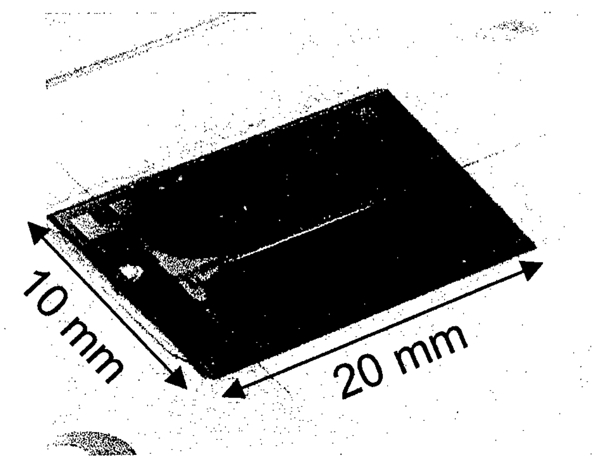
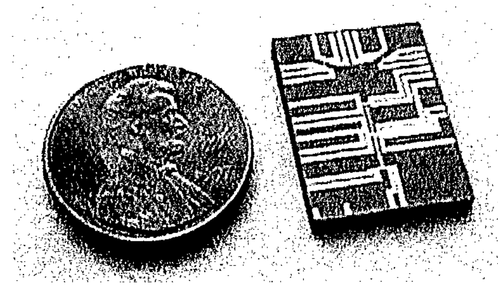
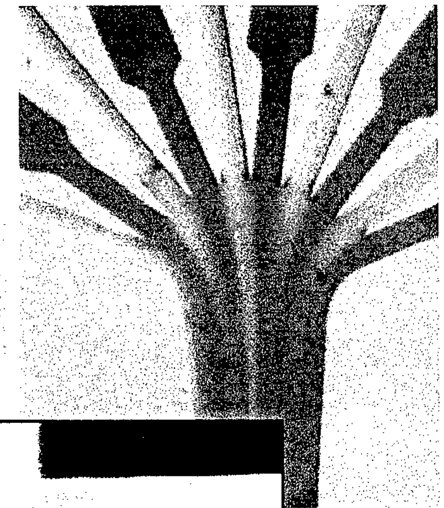
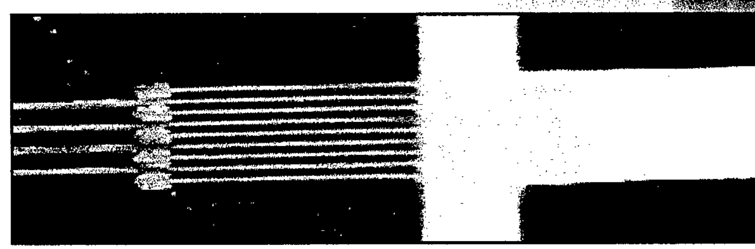
DARPA Microflumes Program (F30602-97-2-0100)

Microchemical Systems - Motivation









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- Potential advantages:
  - High throughput reaction/catalyst screening - combinatorial chemistry
  - Integration of sensors and actuators
  - Improved chemical performance - operation in small dimensions
  - Improve heat and mass transfer - fast thermal cycles
  - Distributed manufacturing - on demand production of toxic intermediates
  - Fast scale-up to production by replication

Motivation for Microchemical Systems

Fabrication of structures with small feature sizes with high aspect ratios enables improved:

-- thermal control (critical for exothermic reactions)

-- fluid mixing via. high contact areas

Integrated sensing that gives more information on the local environment

-- temperature sensors

-- flow sensors

-- pressure transducers

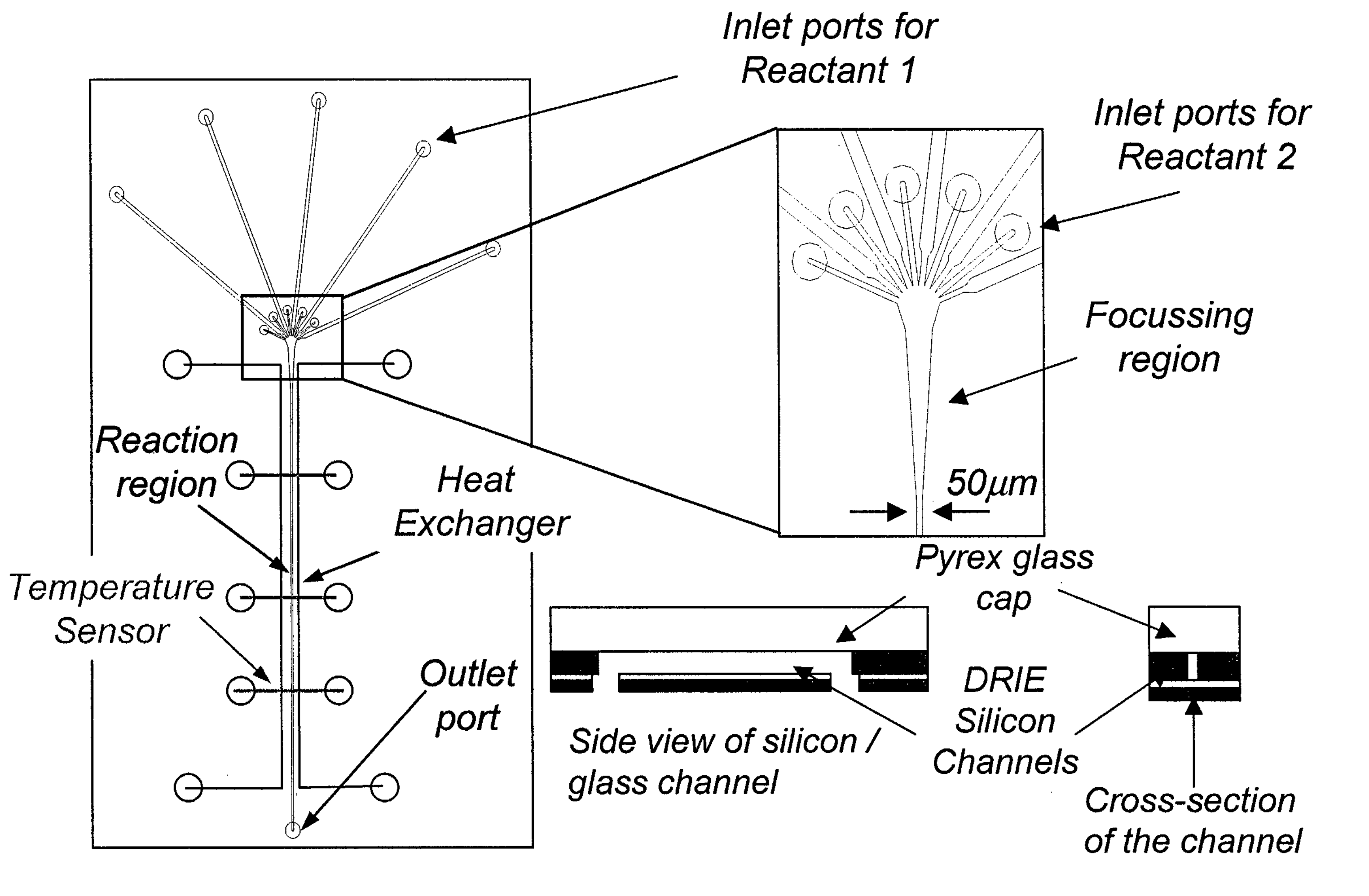
Parallel operation of multiple units

-- distributed, on-demand manufacturing

-- modular, flexible capital equipment

-- safer operation

Design for Liquid-Phase Microreactor



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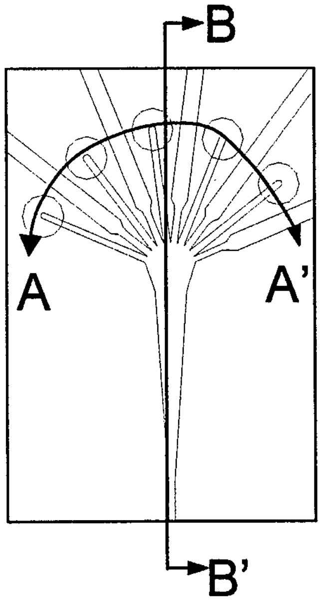
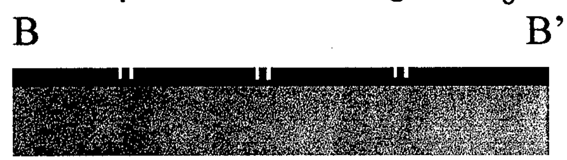
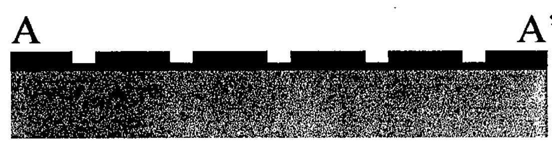
Fabrication Sequence for Liquid-Phase Microreactors



Dope the wafer using $POCl_3$



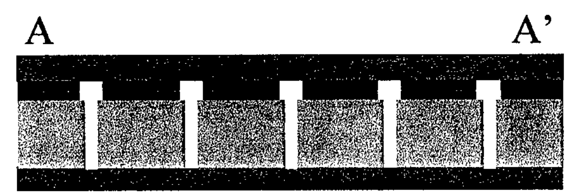
Pattern and etch the temperature sensors in the thin film silicon



Pattern and etch the inlet ports in the thin film silicon

BOE to remove the oxide from the inlet ports

Pattern and etch the mixing and reacting channels in the silicon substrate

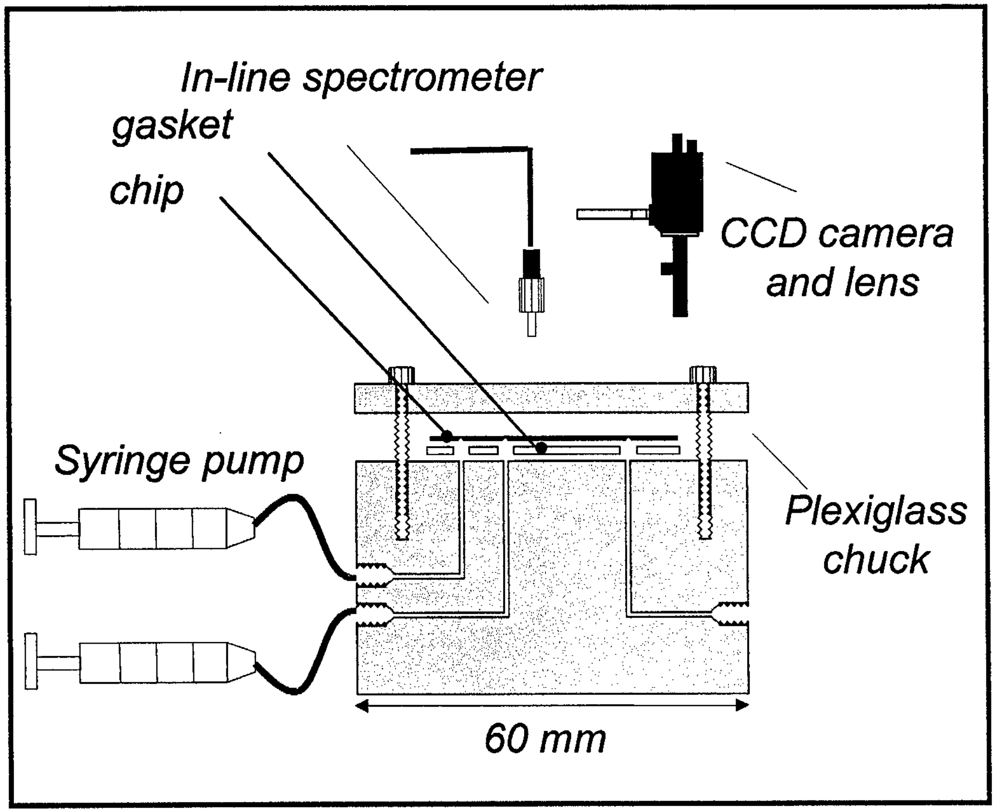


Bond pyrex to the silicon substrate

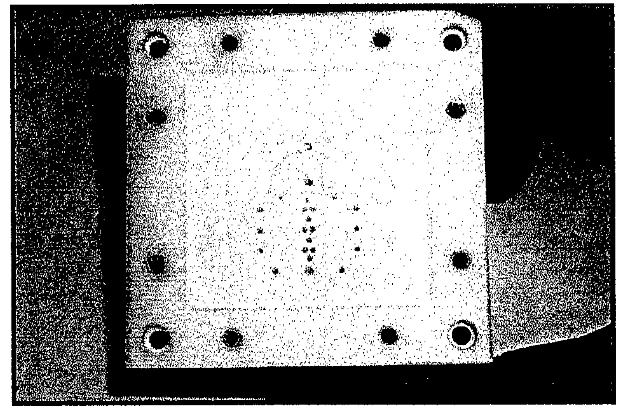
silicon dioxide silicon glass doped silicon

Spectroscopic Station and Packaging

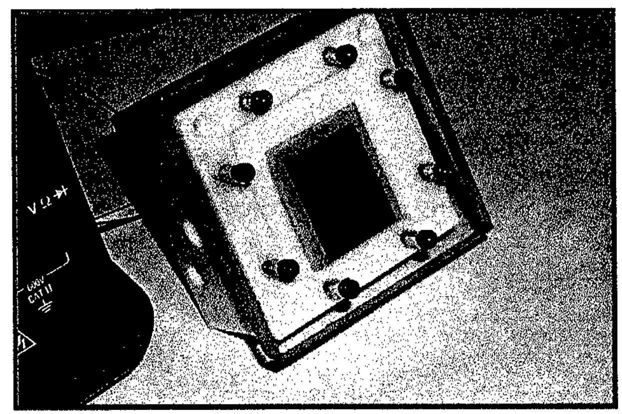
Side View



Front View

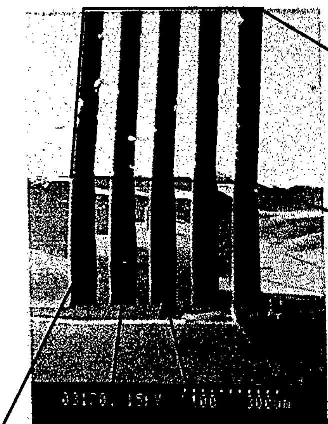


Isometric View

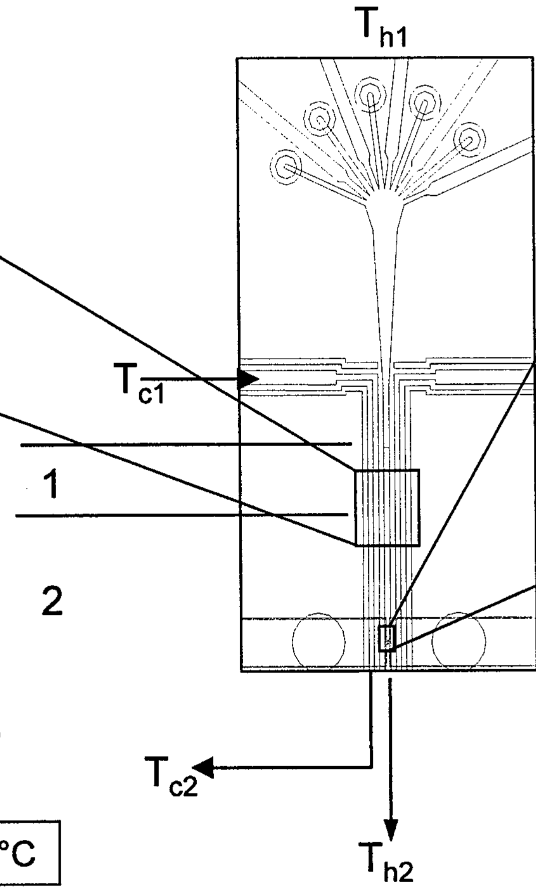


Integrated Heat Exchangers and Temperature Sensors

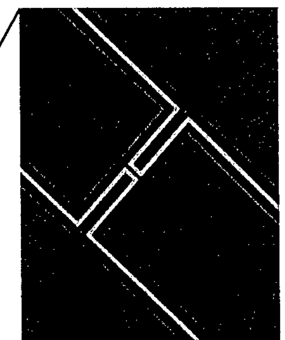
Heat Exchanger



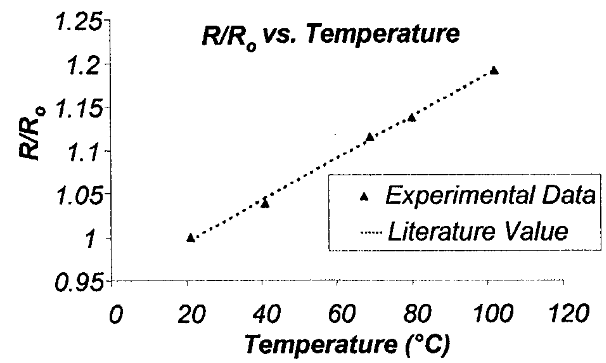
air gap
cooling fluid
reaction mixture



Thin-Film Temperature Sensor



$POCl_3$ doped 2.2 μm silicon film beneath the mixing and reacting channel

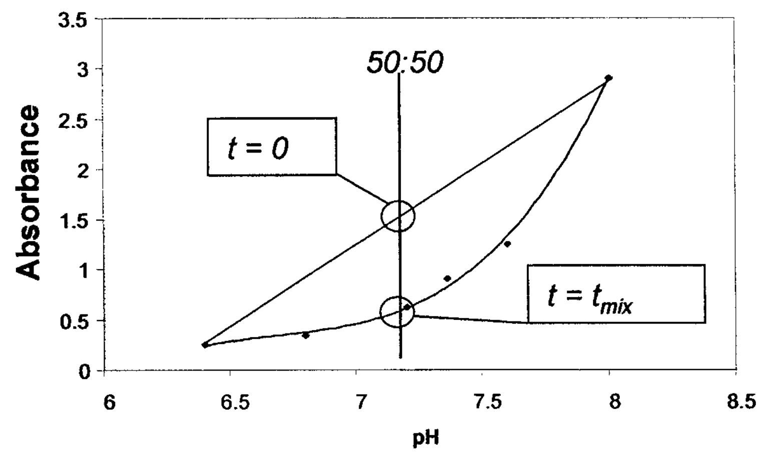


$U_{experimental} = 1500\ W/m^2{}^\circ C$

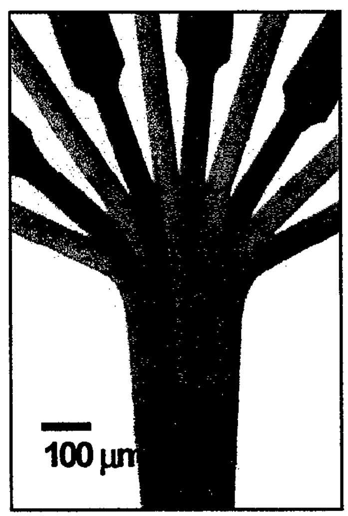
	T_{c2} (C)	σ_{c2}	T_{c1}(C)	σ_{c1}	T_{h2} (C)	σ_{h2}	T_{h1} (C)	σ_{h1}
Run #1	14.87	0.575	11.74	0.558	15.5	0.77	20.06	0.415
Run #2	15.03	0.426	11.73	0.445	17.71	0.462	20.69	0.536

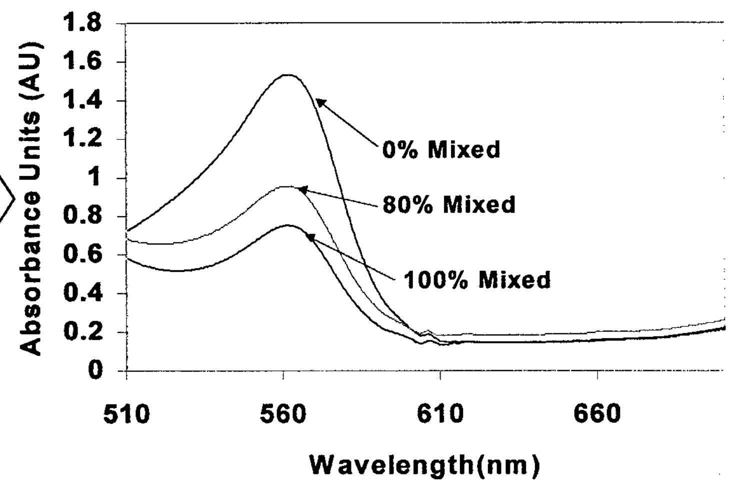
Acid-Base Mixing Study

- Extent of mixing determined by absorbance using phenol red indicator & phosphate buffer
- Mixing proportional to contact time



Experimentally Observed Lamination



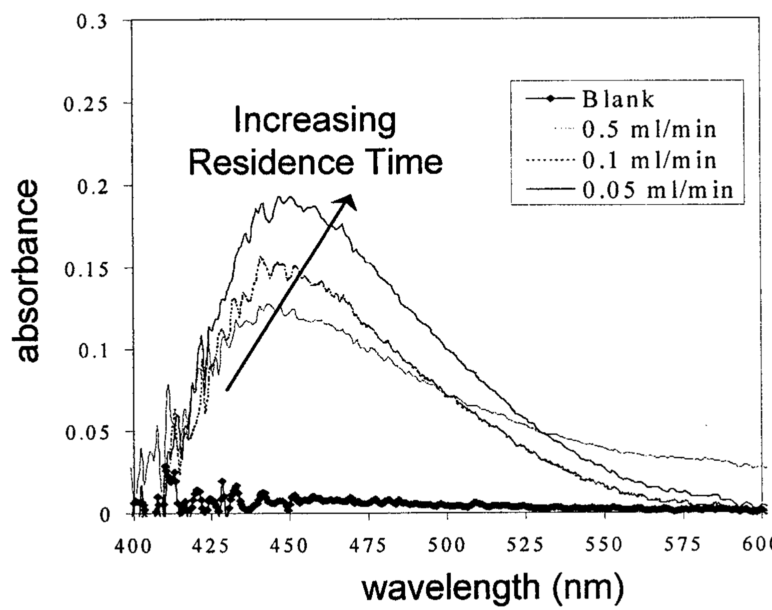


- Experimental mixing time is 10 ms
- Experimental results agree with simulations in CFD-ACE™

Dushman Reaction (Reverse Hydrolysis of Iodine)

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3\,H_2O$$

$$I_2 + I^- = I_3^-$$



- Extended reaction capabilities from the acid-base reaction for the mixing study to production of a molecular species
- Integrated visible spectrometry for on-chip detection

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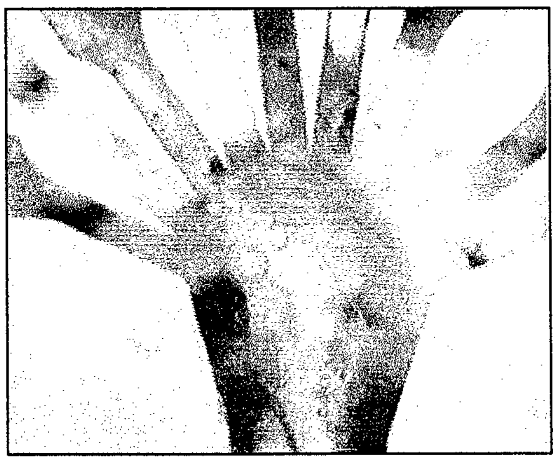
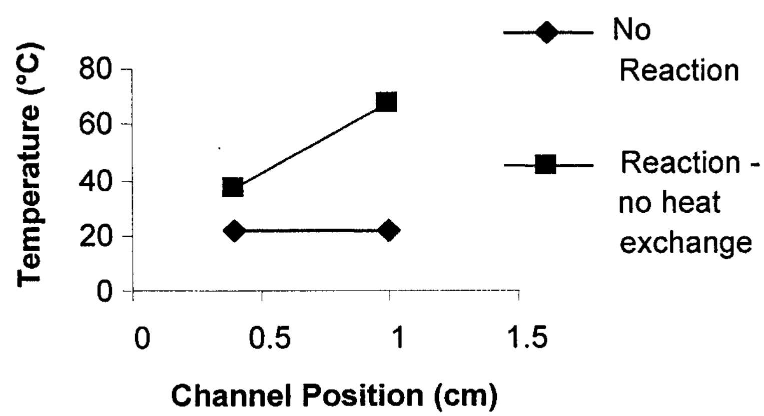
Propionyl Chloride Hydrolysis

$CH_3CH_2\text{-}C(=O)\text{-}Cl + NaOH \rightarrow CH_3CH_2\text{-}C(=O)\text{-}OH + Na^+ + Cl^-$

Visualization of Hydrolysis



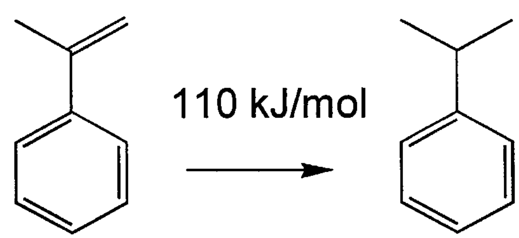
Temperature Profile for Propionyl Chloride Hydrolysis



- Safely contacted and mixed peroxide precursors
- Controlled the temperature using heat exchangers to avoid runaway reaction and decomposition

Opportunities for Multiphase Reactions

- Three-phase gas-liquid-solid reactions can be limited by mass transfer effects.
  -- Hydrogen has a low solubility in most liquids, so efficient mixing and high pressures are required
  -- Controlled distribution of both phases over the catalyst is crucial



α–methylstyrene hydrogenation

- High surface-to-volume ratios available in microfabricated structures can improve gas-liquid absorption by increasing the interfacial contact area

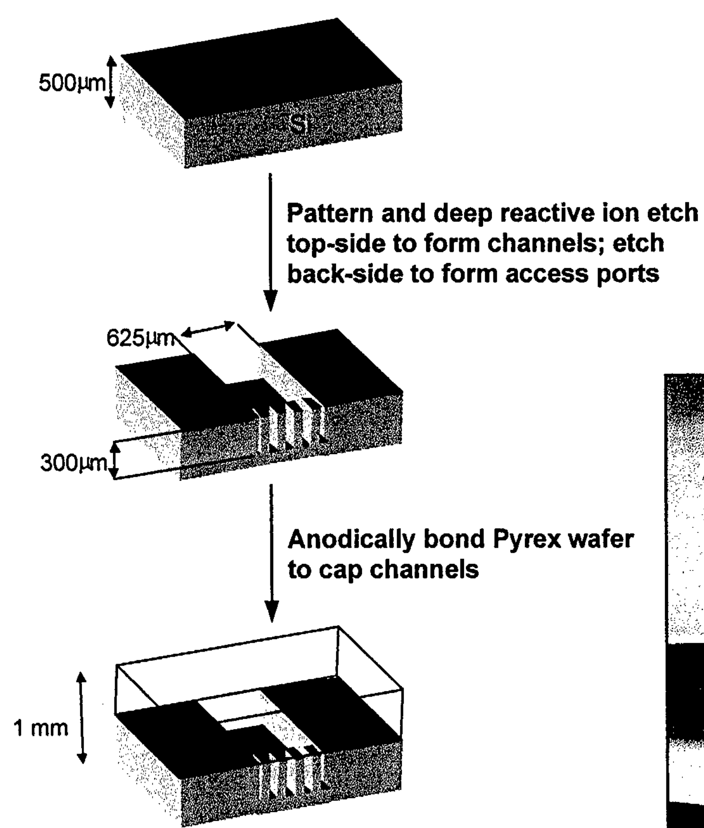
- Smaller characteristic lengths can reduce diffusional limitations either in the liquid or within the pores of the catalyst

Motivation for Micro-Packed Beds

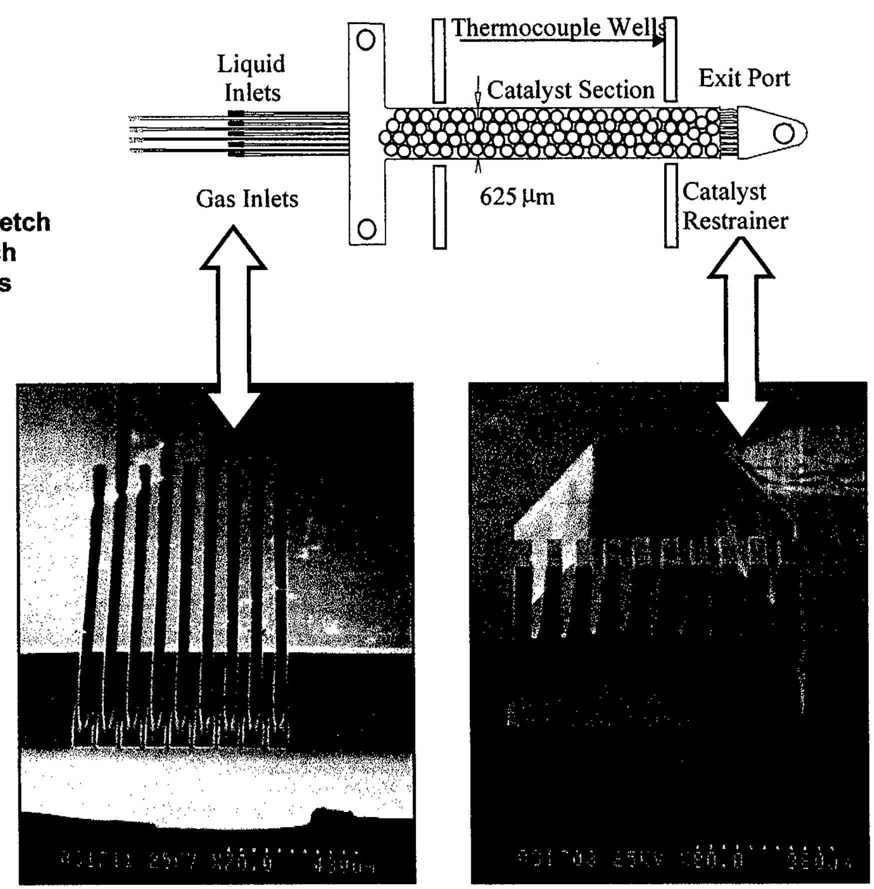
- Need to maximize the number of active catalytic sites per reactor critical for studying chemistries with moderate reaction rates
- Porous supports provide the necessary surface area that thin film catalysts lack, but are more difficult to integrate
- Traditional catalytic packed-beds suffer from reduced thermal conductivity that gives rise to uneven temperature distribution
- Microreactor configurations can improve thermal control and multichannel configurations can reduce pressure limitations for small particle catalysts

Multi-Phase Microreactor Design and Fabrication

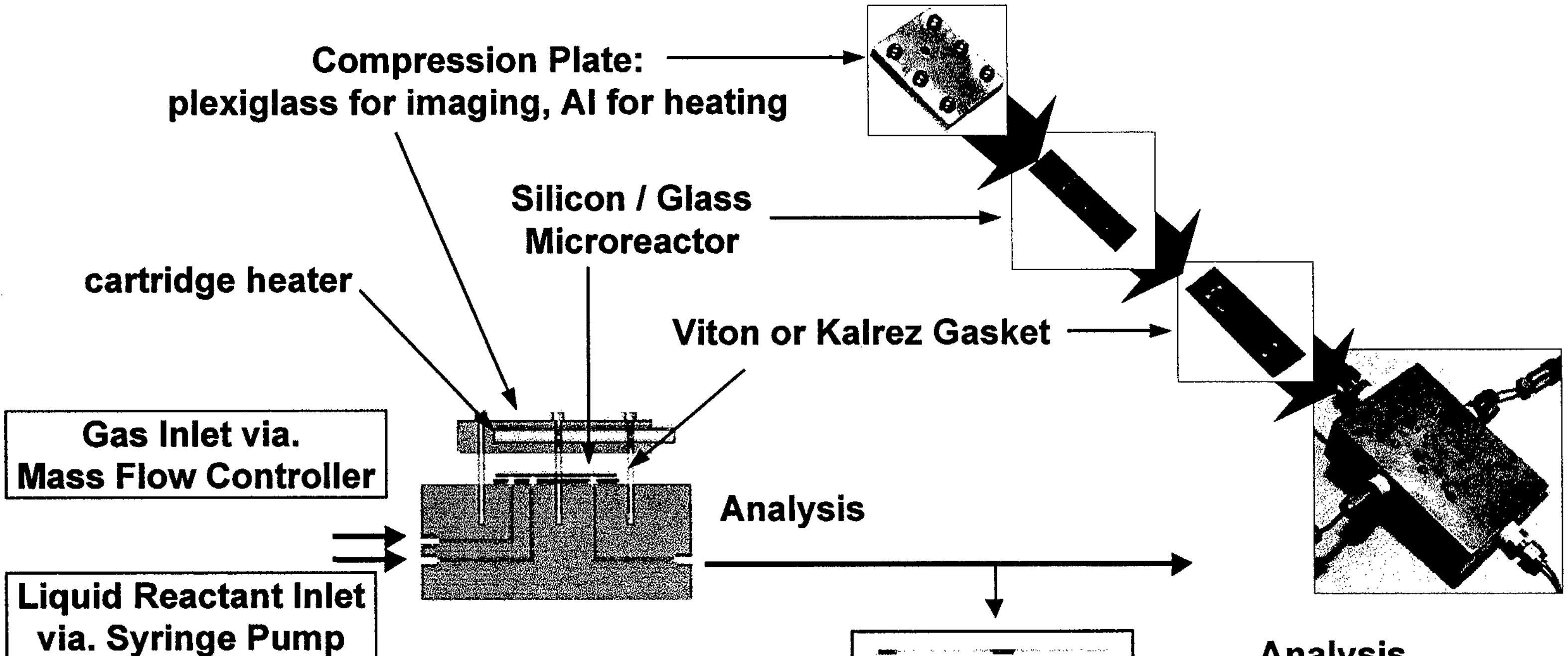
Fabrication Scheme

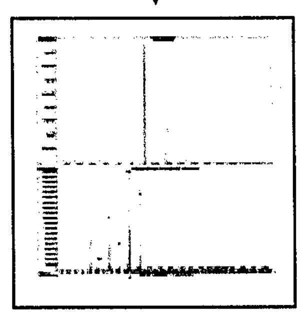


Reactor Design



Reactor Packaging and Experimental Set-up



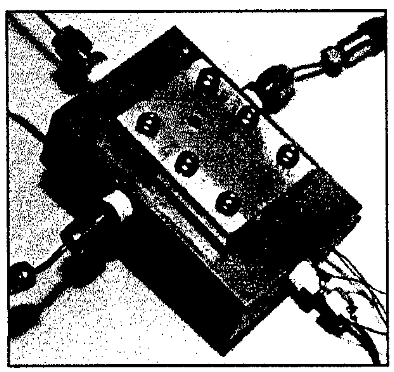


Analysis

Chip temperature monitored with in situ thermocouples

Liquid products analyzed off-line using GC-MS

Gas products analyzed on-line using MS



Packaged Microreactor

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Heterogeneous Gas-Phase Reaction in a Micro Packed-Bed Reactor

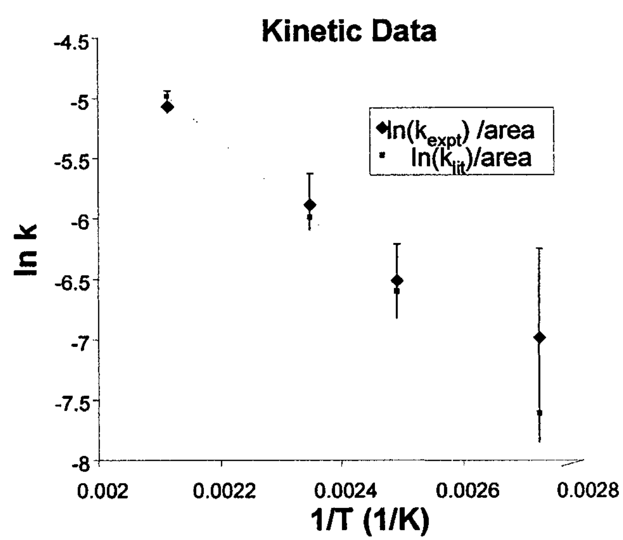
Phosgene production: $CO + Cl_2 \longrightarrow COCl_2$ $\Delta H = -109$ kJ/mol

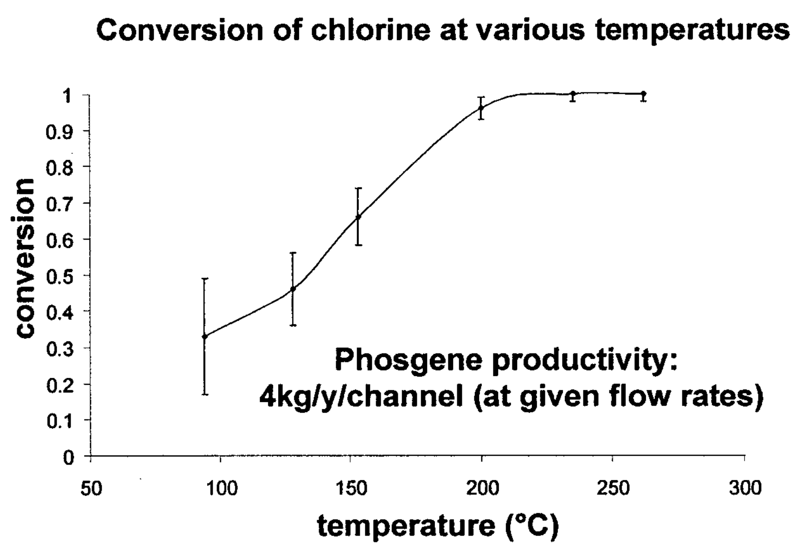
- Important industrial intermediate
- Moderate to fast reaction

- Exothermic, dangerous reaction!
- Operating range 150-400°C
- Highly toxic product (0.1 ppm TLV)
- Hazardous shipping

<u>Excellent point-of-use candidate for on-site, on-demand production</u>

Preliminary Results





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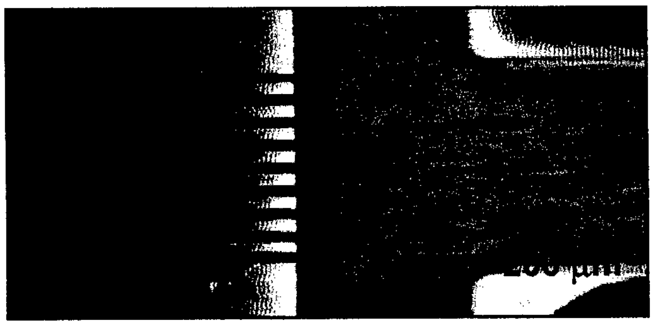
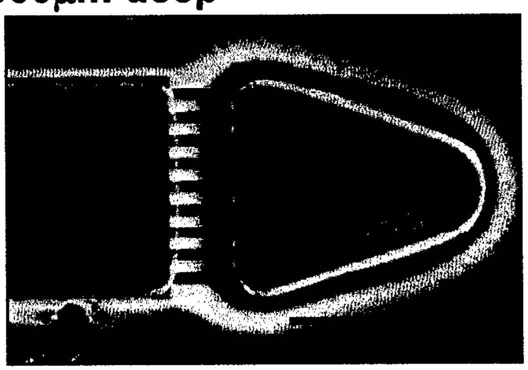
Visualization of Gas / Liquid Contacting

Water / dye solution in an unpacked channel

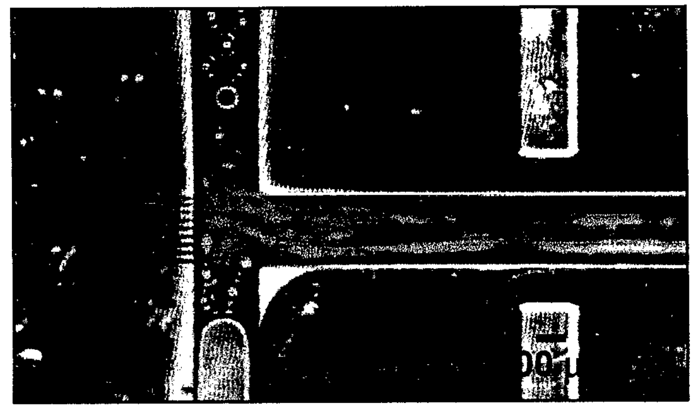
Water only flow

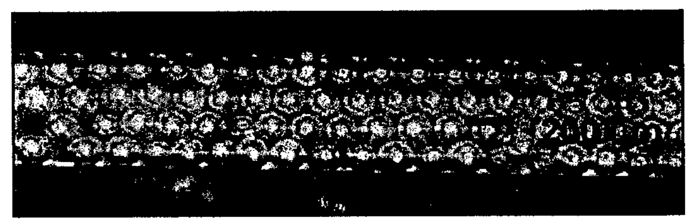


9 Inlet Channels: 25μm wide, 300μm deep



Air / water co-current flow



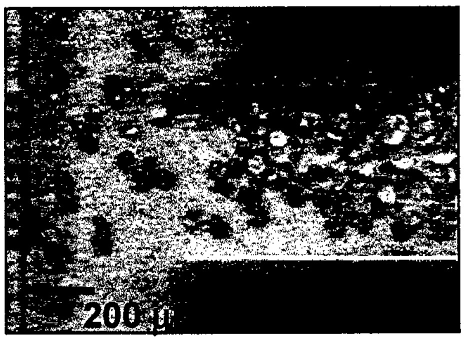


Foam formation using air, H_2O and surfactant

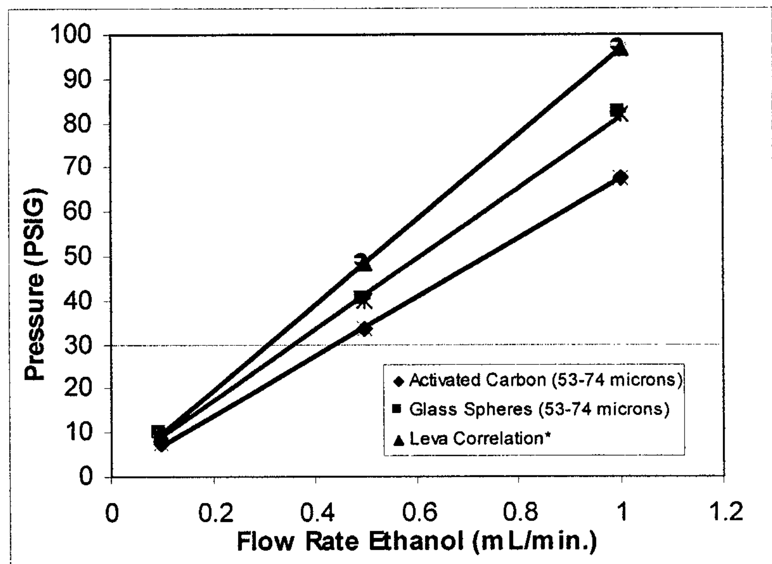
Pressure Drop for Microfluidic Packed Beds: Calculations and Experimental Results

Correlations such as Ergun's equation or Leva's correlation for pressure drop in packed beds (Re'<10):

$$\frac{\Delta P}{L} \propto \frac{\mu \cdot Q}{D_p^{\,2} \cdot A_s} \cdot \frac{(1-\varepsilon)^2}{\varepsilon^3}$$



50 µm glass microspheres as packing

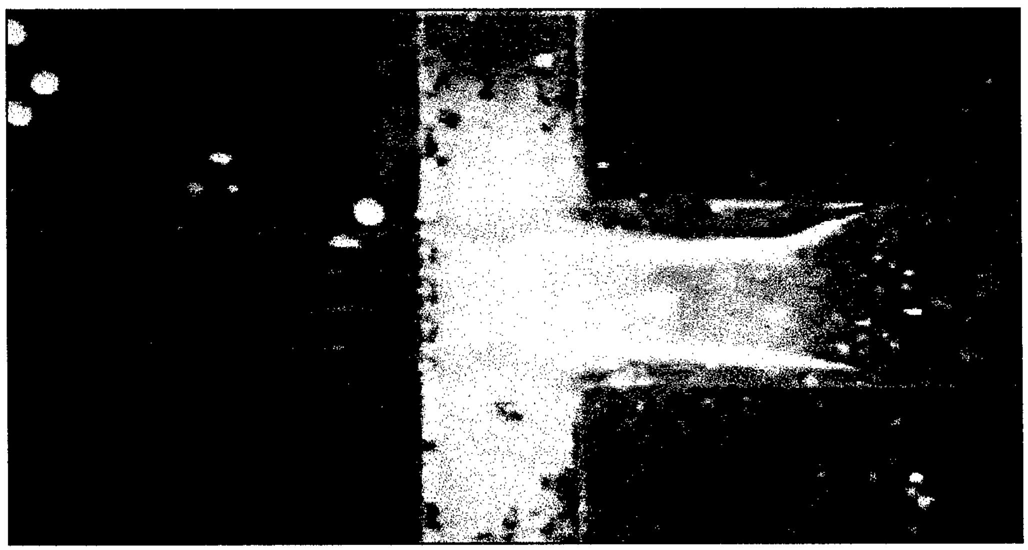


- Measured pressure drop agrees with correlation
- Depends strongly on: void fraction & shape and distribution of particles

Heterogeneous Multiphase Reaction in a Micro Packed-Bed Reactor

- Performed multiphase hydrogenation reactions
- Reaction rates up to 0.01 mmol/min per reaction channel at 50°C and 5atm

$$\alpha\text{-methylstyrene} \xrightarrow[\text{Pd /C}]{H_2,\ 311\text{ K}} \text{cumene}$$



Co-current flow of H_2 with heptane over a packed bed of carbon particles

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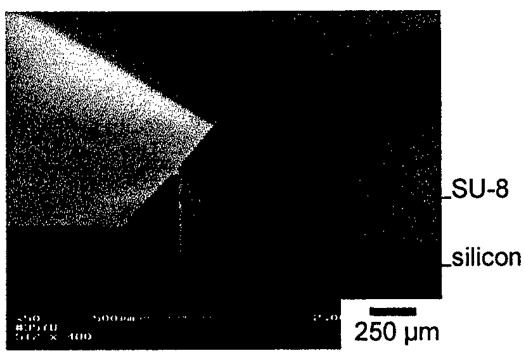
Hybrid Microreactors

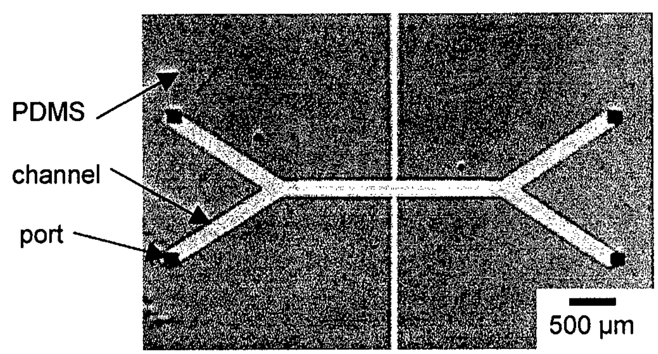
The combination of standard microfabrication techniques with unconventional methods and materials for fabrication (e.g. soft lithography, SU-8):

- Allows the fabrication of microreactors in a variety of materials (polymers, ceramics) other than silicon, silicon dioxide, silicon nitride
- Enables chemical reactions to be run that are not compatible with silicon
- Permits the fabrication of 3D structures that would otherwise be difficult to produce
- Can produce structures that can be replicated without access to a cleanroom

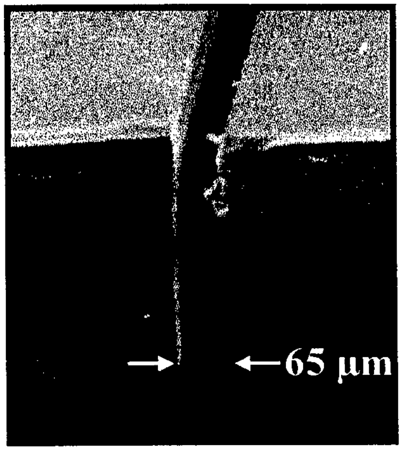
Microchannel formed by Deep Reactive Ion Etching and patterned using SU-8 resist



Microchannels formed by sealing PDMS against nitride-coated wafer with access ports

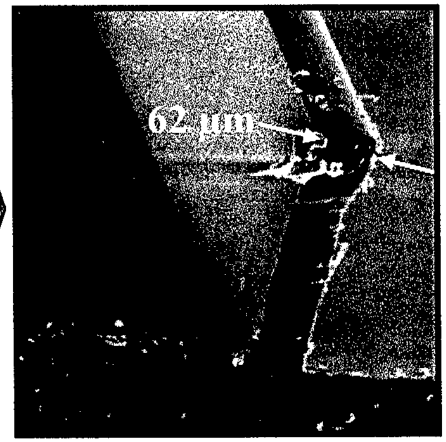


Micromolding Microfluidic Channels



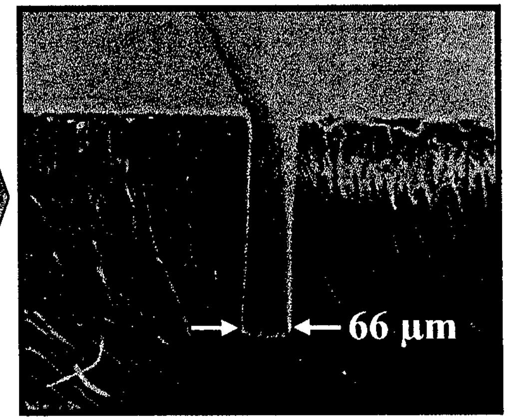
Si Master

- •STS Etch Silicon
- •Treat silicon with surface passivating agent



PDMS Mold

- •Mix curing agent and elastomer thin fill the mold.
- •Evacuate to remove trapped air. Cure at 75 C for 2 hours
- •Produces flexible replica of silicon features



Epoxy Reactor

- •Cast UV-curable epoxy over PDMS mold.
- •Cure and remove mold

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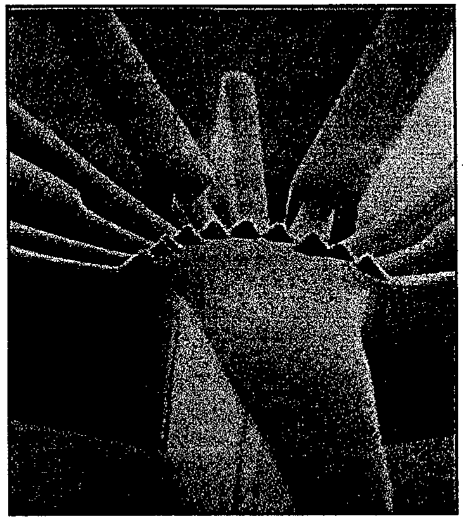
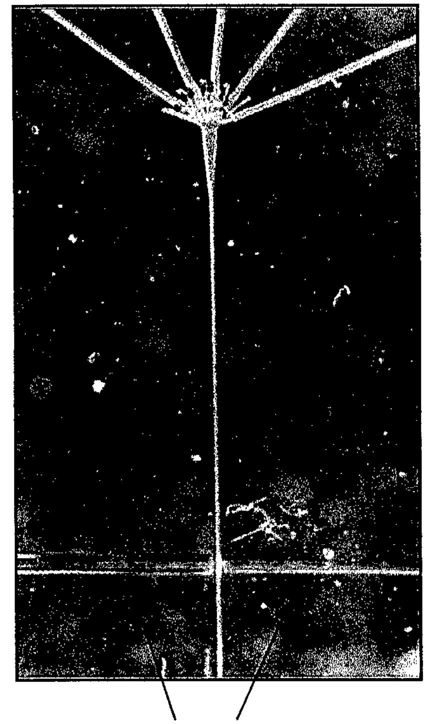
Micromolded Liquid Microreactors

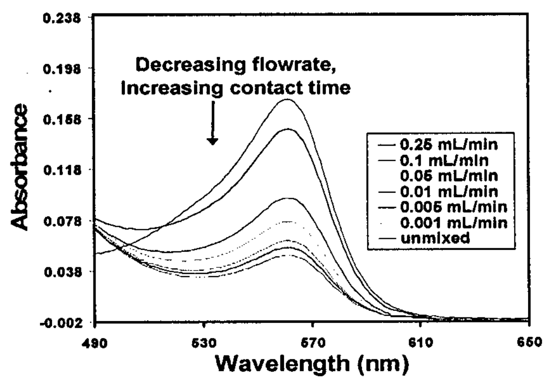
SEM of PDMS mold from silicon microreactor





Optical fibers for source and signal acquisition

In-Situ Visible Spectroscopy



Accomplishments

Liquid-Phase Microreactors:

- Designed and fabricated liquid-phase microreactor
- Demonstrated fast mixing, good heat transfer, and integrated temperature sensing
- Showed safe handling of reactive reagents (e.g., acid chloride)
- Performed model chemical reactions in microreactors (acid chloride hydrolysis and reverse hydrolysis of iodine)

Multi-Phase Microreactors:

- Fabricated microfluidic devices for catalytic heterogeneous chemistries
- Demonstrated multi-phase fluid flow and performance up to 250°C/10 atm
- Performed heterogeneous gas-phase reaction:
  -- phosgene synthesis over packed-bed of carbon particles
- Carried out heterogeneous multi-phase reaction:
  -- hydrogenation of AMS over Pd/C particles

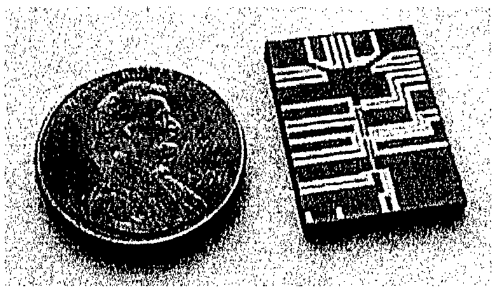
High Temperature Gas Phase Catalytic and Membrane Reactors

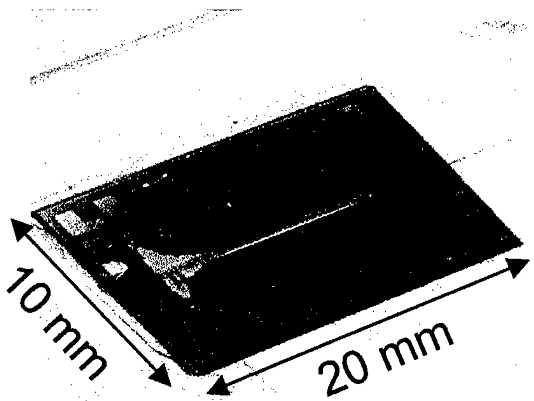
Aleks J. Franz, Sameer K. Ajmera, Samara L. Firebaugh, David Quiram, Klavs F. Jensen, Martin A. Schmidt

DARPA MicroFlumes Program

MIT

Motivation for Chemical Process Miniaturization

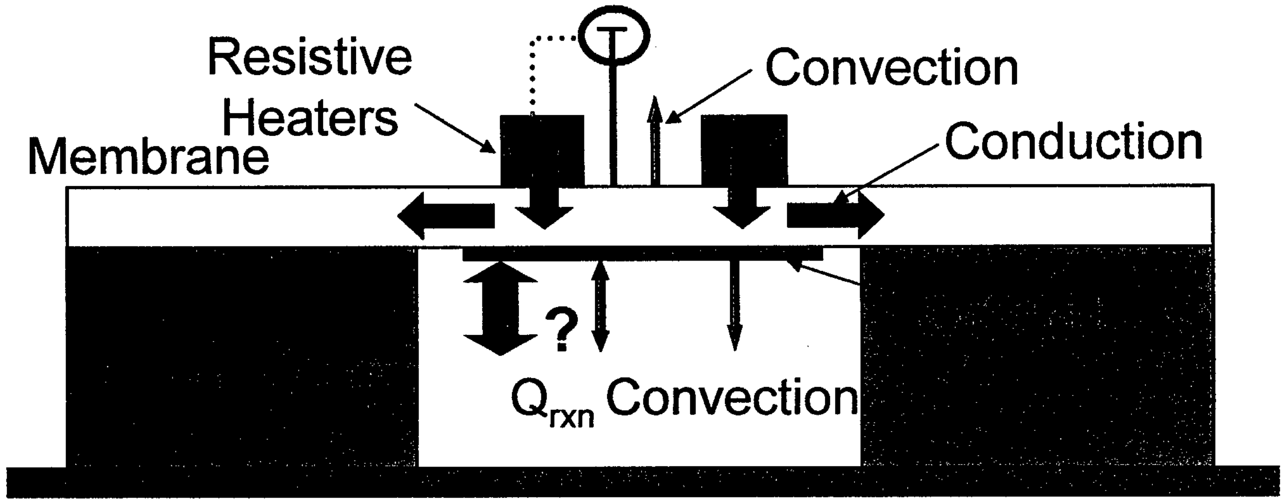




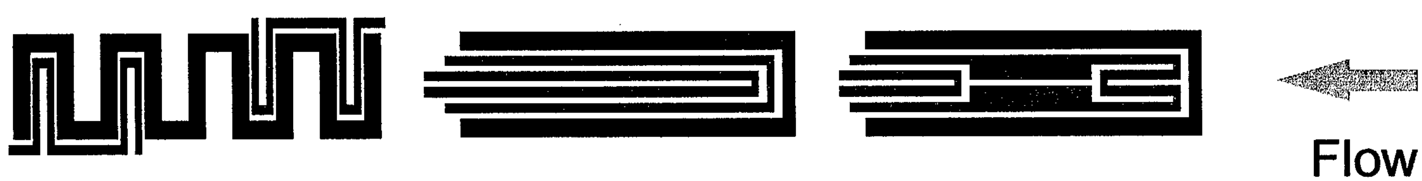
○ Potential advantages:

- Safer operation in small dimensions
- Improved chemical performance
- Process intensification
- Distributed manufacturing - on demand production of toxic intermediates
- Fast scale-up to production by replication
- High throughput reaction/catalyst screening - combinatorial chemistry
- Miniaturized chemical systems
- Novel analytical capabilities

Microreactor Design Flexibility

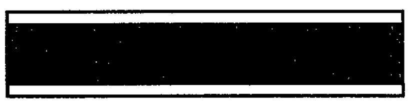


- Heat flux in the microreactor can be controlled through straight forward membrane and heater design modifications.
- Photolithographically patterned heaters and temperature sensors allow for great flexibility, reaction specific design, and integration of flow sensors.



SiN Microreactor Fabrication Process

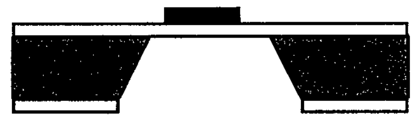
Starting material: Si wafer coated with **1 µm** of SiN



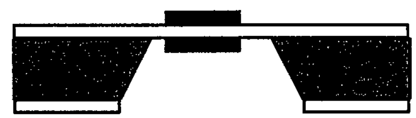
Pattern and plasma etch SiN on backside to expose underlying Si

Pattern Pt heaters and TSRs on front side using IR alignment and metal lift-off

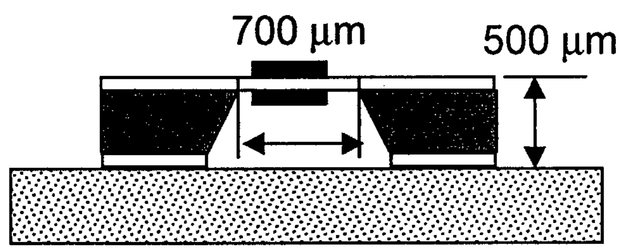
Etch channel using KOH to define SiN membrane

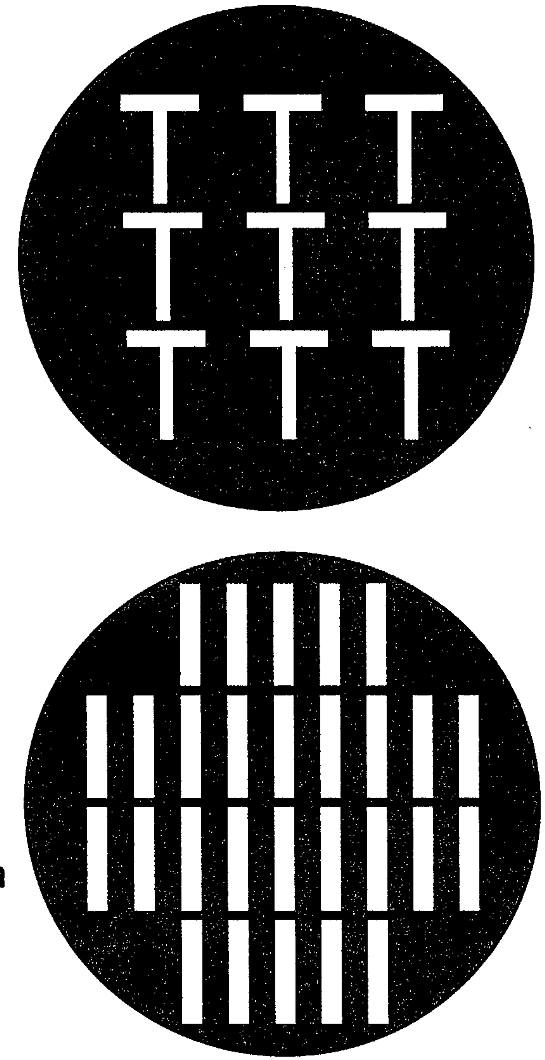


E-beam evaporate Pt catalyst in channel via shadow mask



Cut chips and bond to Al sealing plate





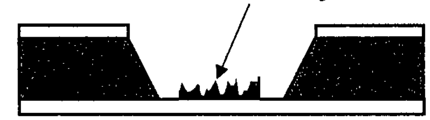
Catalyst Preparation

- Thin-film approach

E-beam evaporate catalyst into channel via shadow mask

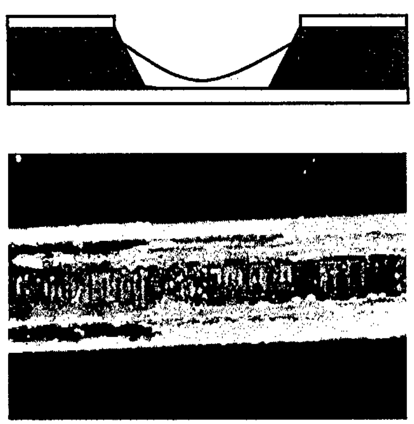
Thermally treat to activate catalyst

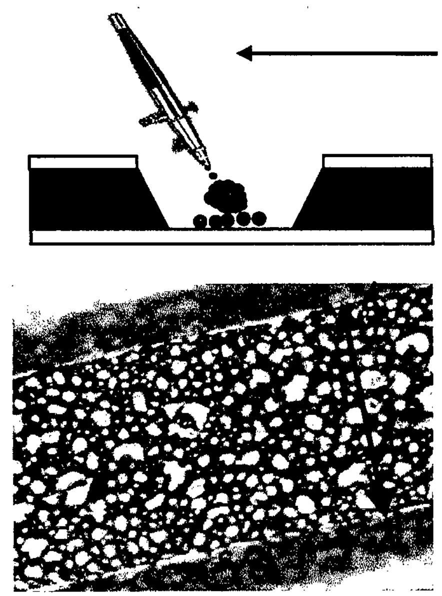
Roughened / active catalyst surface



- Conventional "wet chemistry" approach
  - Higher surface area- higher activity - mixed oxide catalysts

Surface tension effects cause catalysts to be concentrated along side-walls





Artist's Airbrush

Use an atomizer to generate fine droplets

~700 μm

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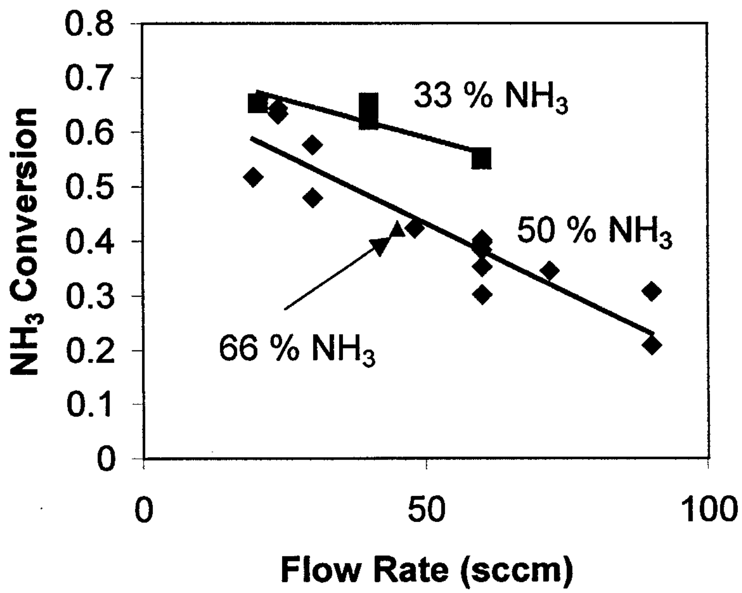
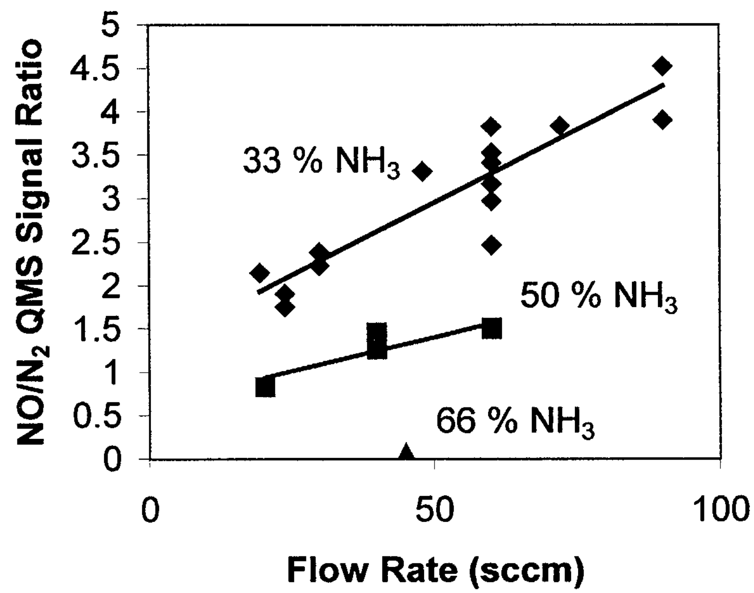
Reactions and Catalysts Used in Microreactor





- Autothermal microreactor operation and classic conversion/ selectivity trade-off observed for ammonia oxidation over platinum.
- Other deposited catalysts: mixed vanadium oxide, iron, palladium, silver, nickel, iridium, rhodium, carbon.
- Other reactions: ammonia decomposition, methane partial oxidation, ethylene hydrogenation, oxidation of hydrogen, carbon monoxide, ethylene, propane.

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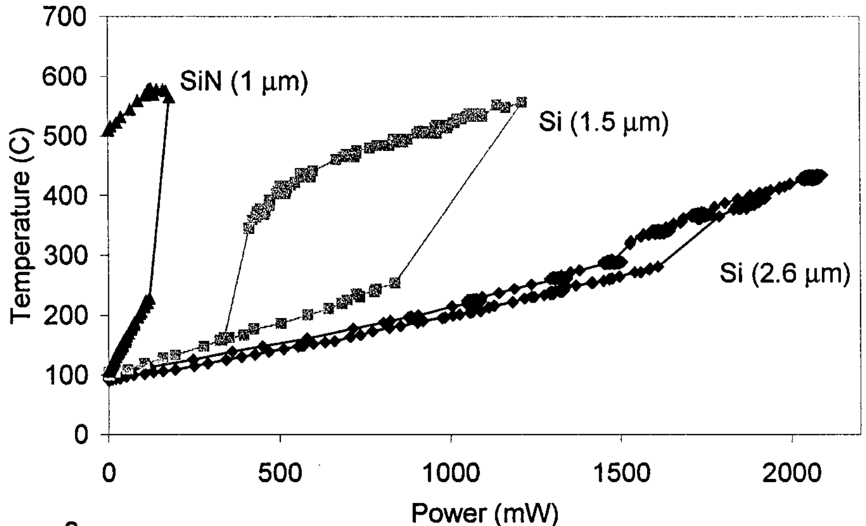
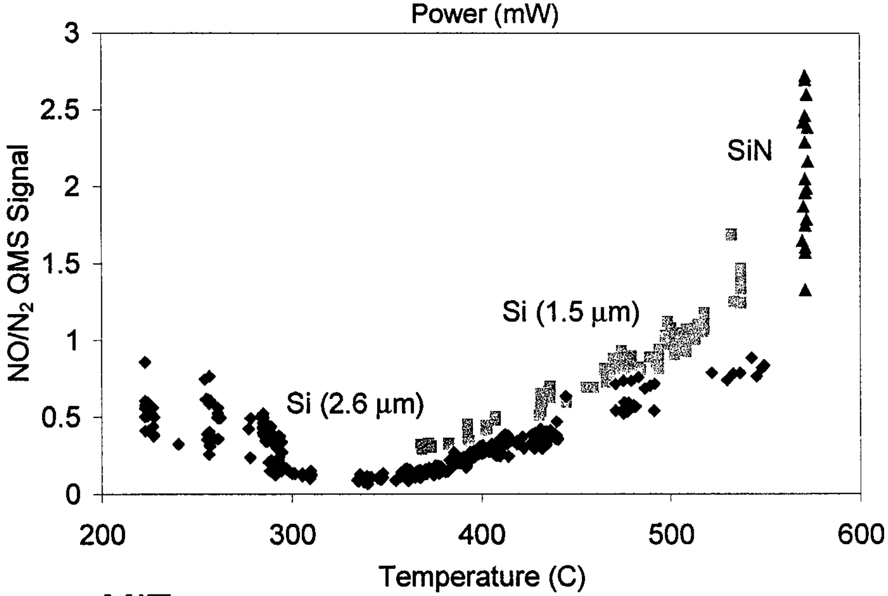
Effect of Membrane Properties on Reactor Behavior for Ammonia Oxidation





- Increasing ability of membrane to dissipate heat expands thermal operating range of the microreactor!
- The increased thermal operating range leads to an increased control over reaction selectivity!

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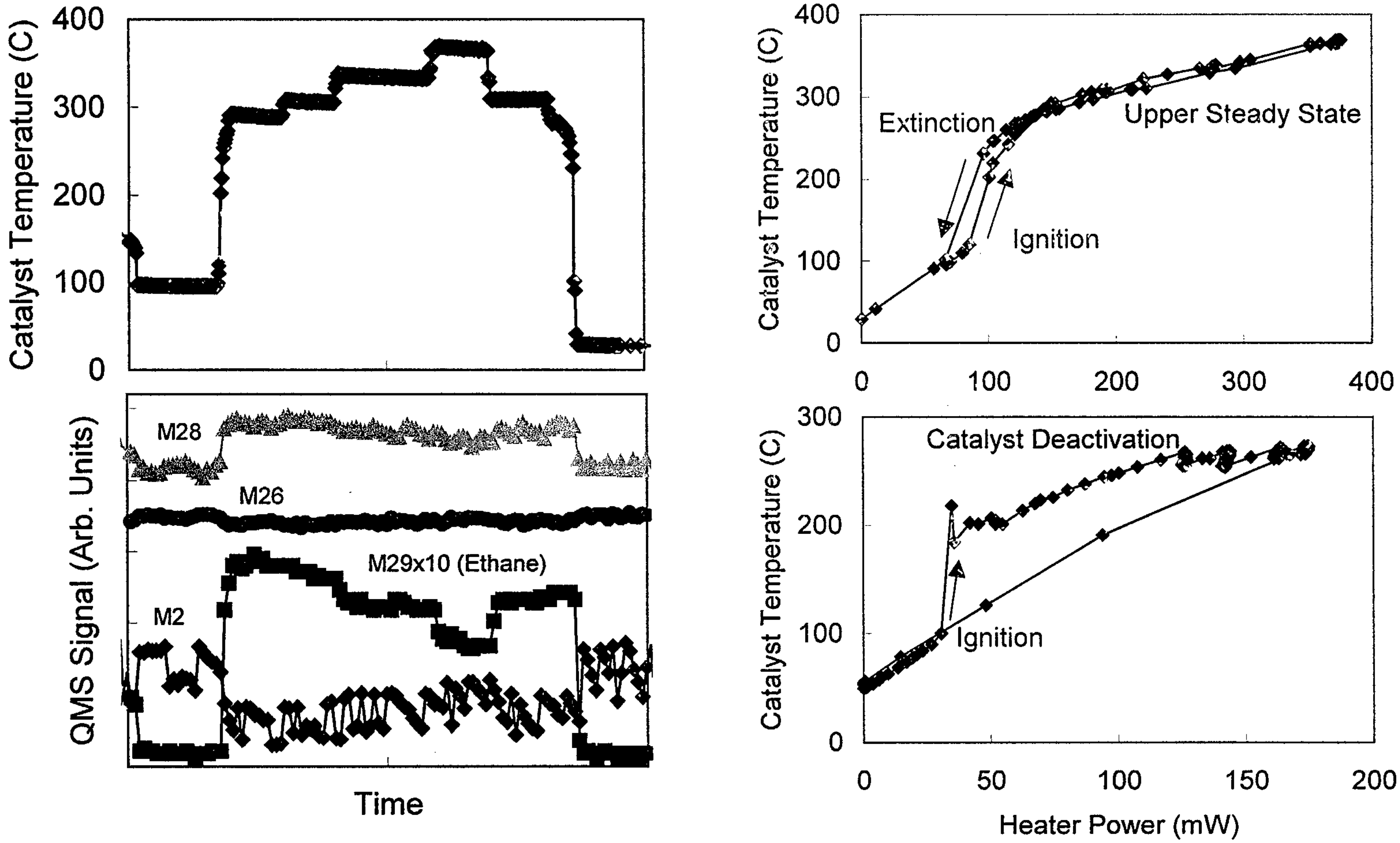
Ethylene Hydrogenation Over Palladium



- Ethylene hydrogenation carried out using gas phase microreactors.
- Catalyst deactivation observed calorimetrically.

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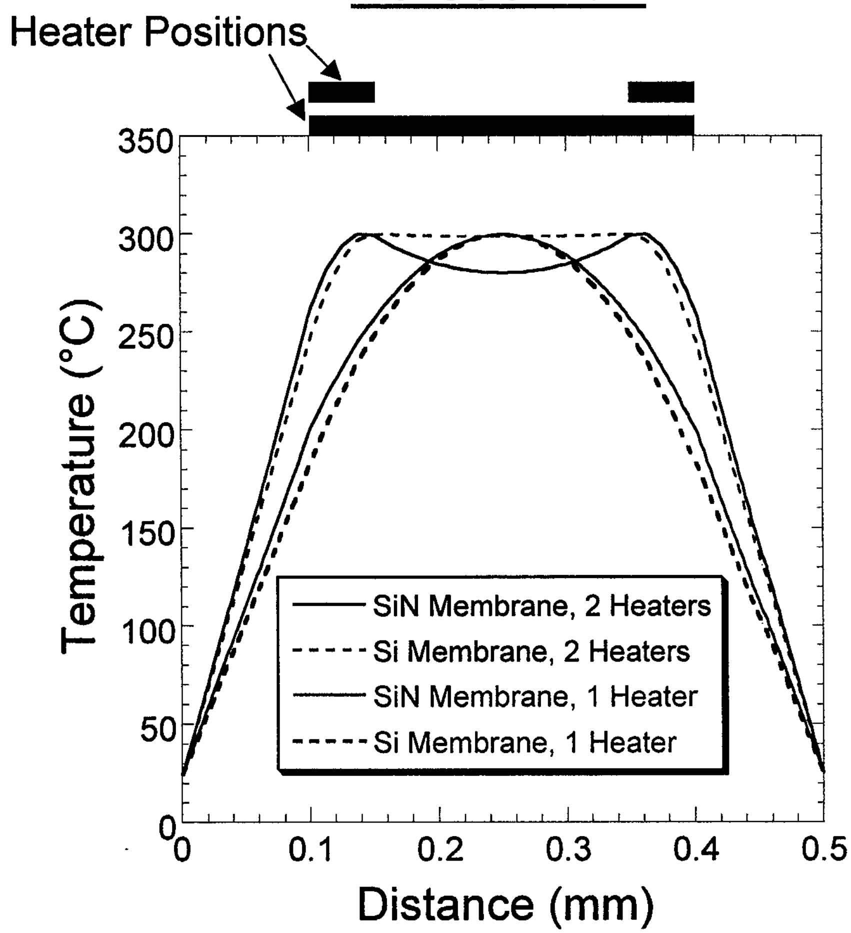
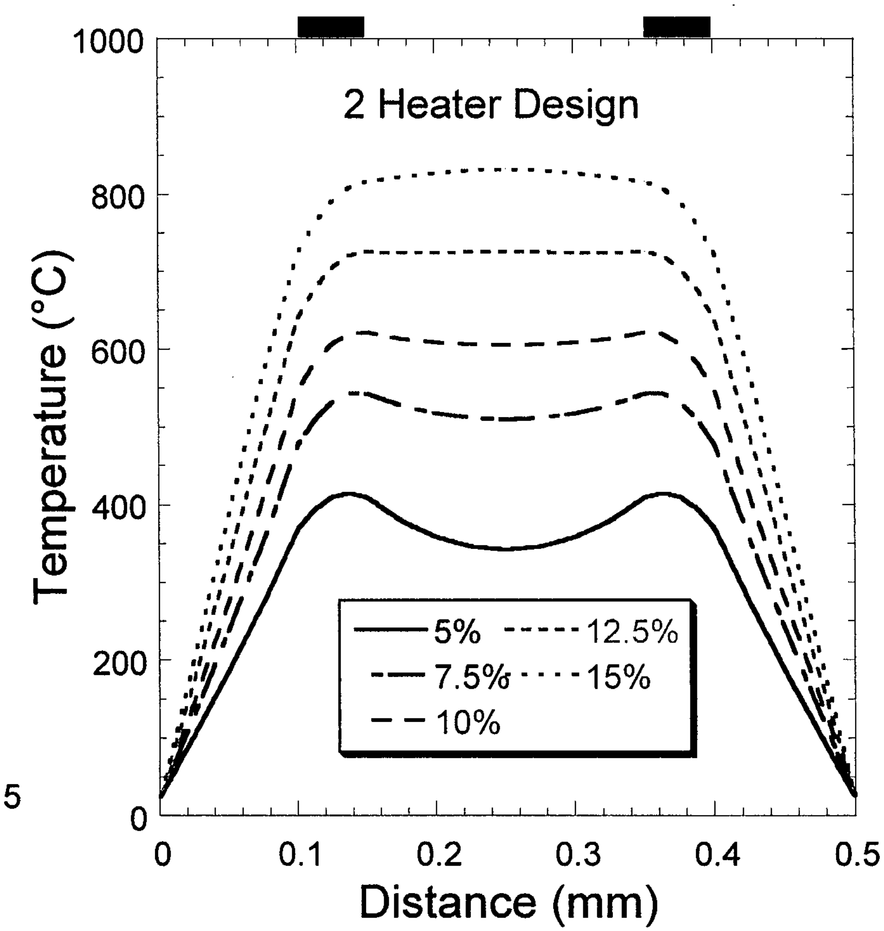
Reactor Temperature Control Through Heater Design

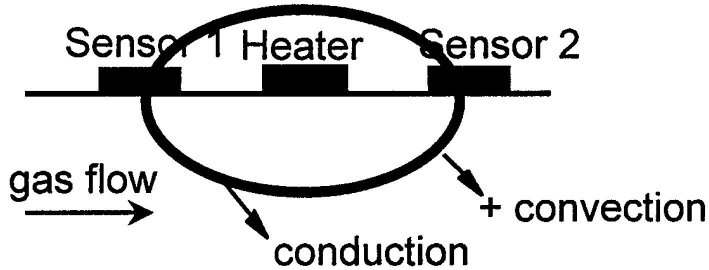
No Gas Flow

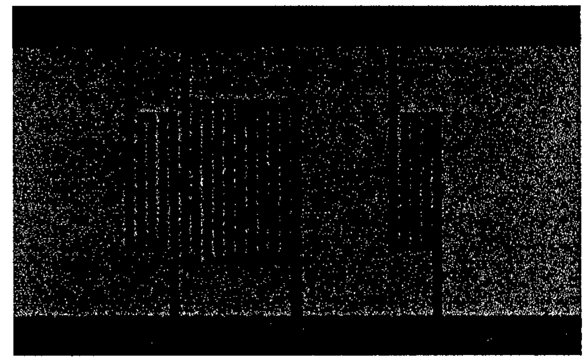


With Gas Flow and Reaction

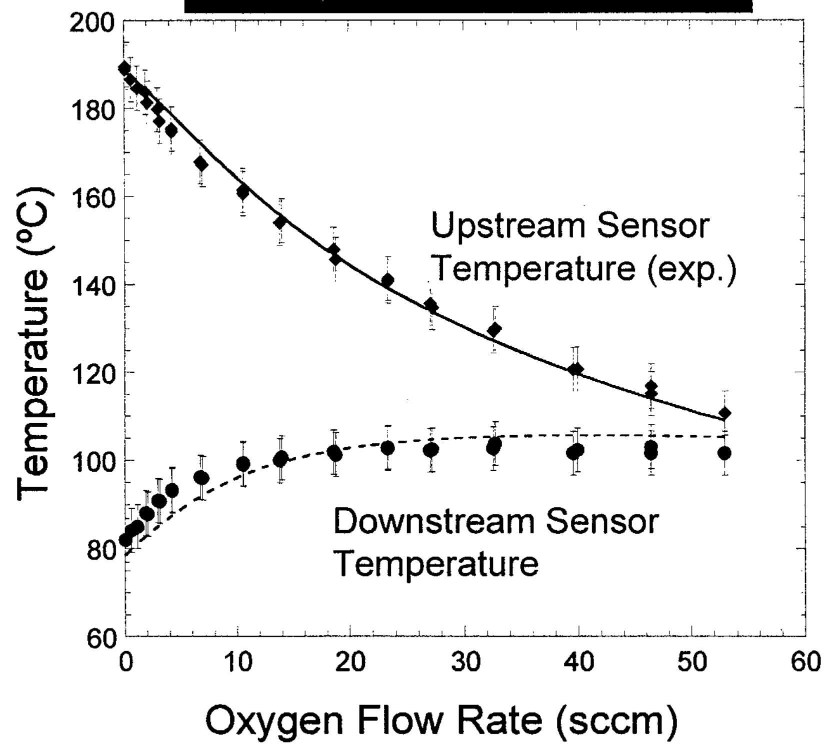


Integration of Flow Anemometers



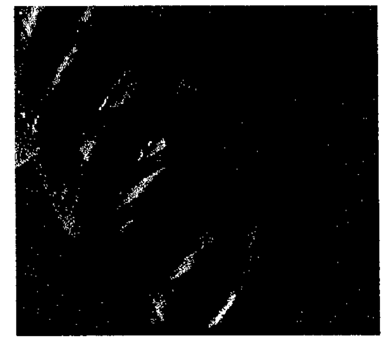


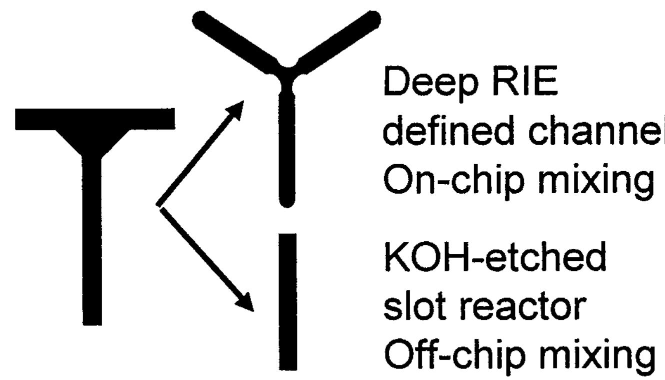
- Goal: Detect flow rate from changes in temperature around a heater
- Problems:
  - Optimum location for the temperature sensor
  - Effect of membrane thermal conductivity and thickness on performance
  - Determine the sensor performance for various gases
  - Effect of heater length and power on performance
- Solution: FEM simulation driven design

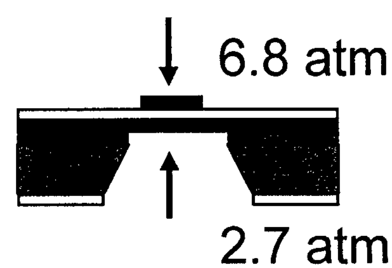


Robustness of Membrane-Based Reactor Design

- Advantages of membrane based design:
  - Integration of sensing/actuation elements
  - Temperature control
- Very thin membranes can be fragile
- Improvements:
  - Reactor membrane geometry
  - Membrane construction (strength, residual stress)
- Results:
  - Buckling eliminated using stress-compensated membranes (Max. T improved from ~650 °C to >800 ° C)
  - New reactor geometries improve structural integrity
  - Rupture pressures:







Motivation for Micro Palladium Membranes

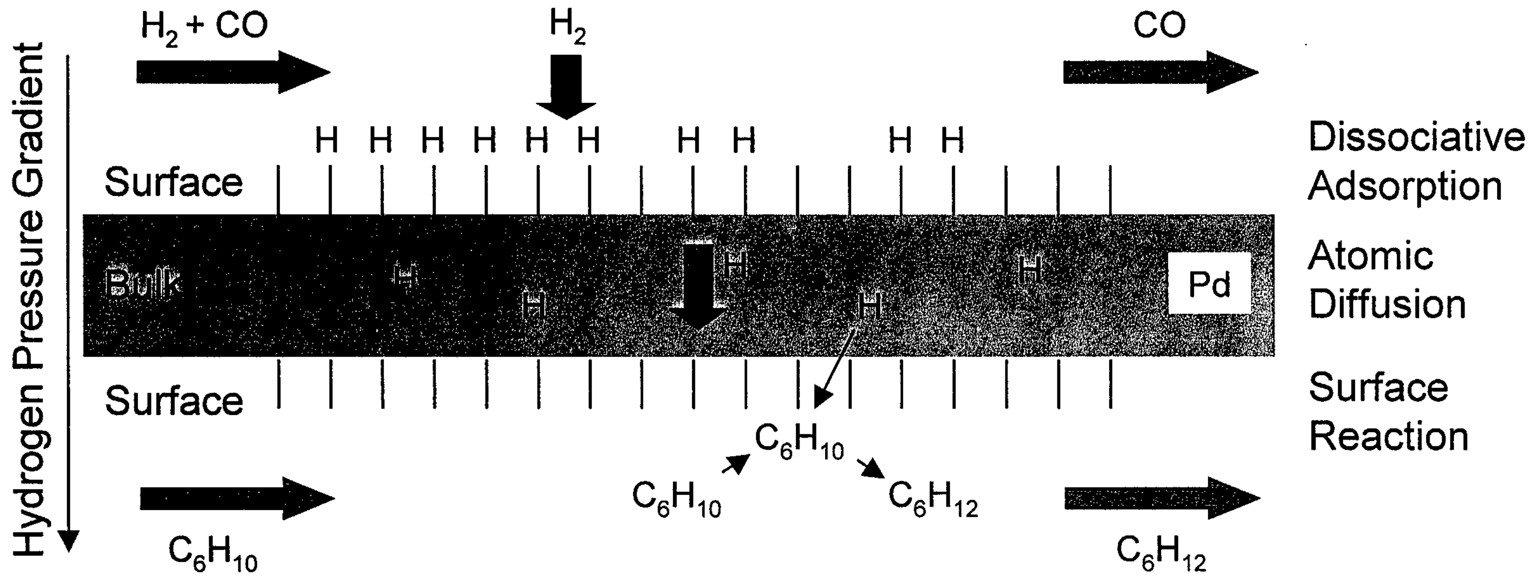
Microchemical System Components

Sampling/Mixing → Reactions → Separations → Sensing/Storage

- Chemical separations are an important feature of chemical processing and few types of separation processes have been successfully miniaturized.
- Palladium membrane reactors offer advantages over conventional reactors, and microfabrication could increase their efficiency.
- Chemical hydrogen generation and purification on a small scale is desirable for mobile/portable fuel cell power generation systems.

Chemical Fuel → H_2 Generation → H_2 Purification → Fuel Cell → Power

Palladium Membrane Operating Principles



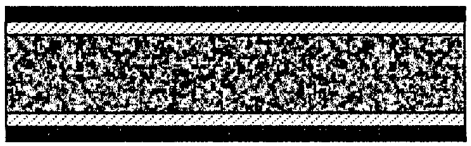
- Hydrogen flux usually rate limited by diffusion:

$$J_H = \frac{F}{l}\left(P_1^{0.5} - P_2^{0.5}\right)\exp\left(\frac{-E_A}{RT}\right)$$

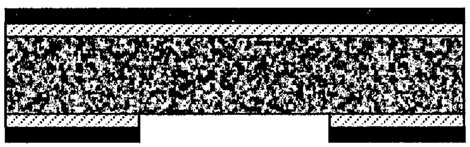
- Hydrogen flux strongly dependant on temperature (T), hydrogen pressure gradient (P_1,P_2), and palladium film thickness (l).
- Membrane design trade-offs between efficient heating, structural strength, and film thickness exist.

Device Fabrication - Silicon Chip

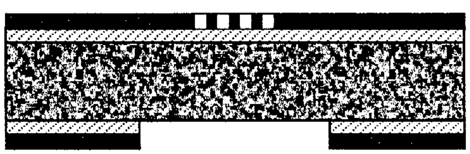
Starting Material: Si wafer with 0.25 µm of oxide and 0.3 µm LPCVD nitride



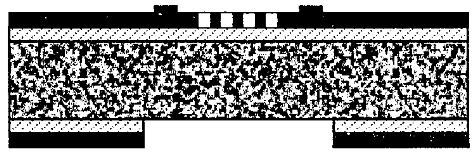
Pattern back side (Dry nitride etch followed by BOE)



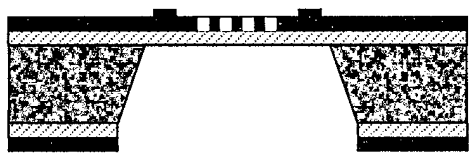
Pattern perforations on front side (Dry nitride etch)



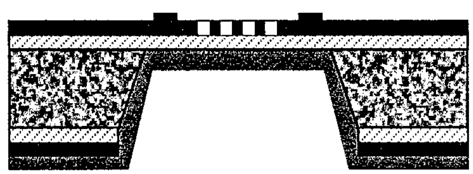
Heater patterning and metallization (Pt/Ti)



Backside KOH etch, to form channel/membrane structure

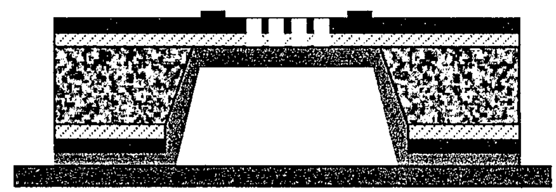


Blanket deposition of Pd (.2 µm) with a thin Ti (.01 µm) adhesion layer.

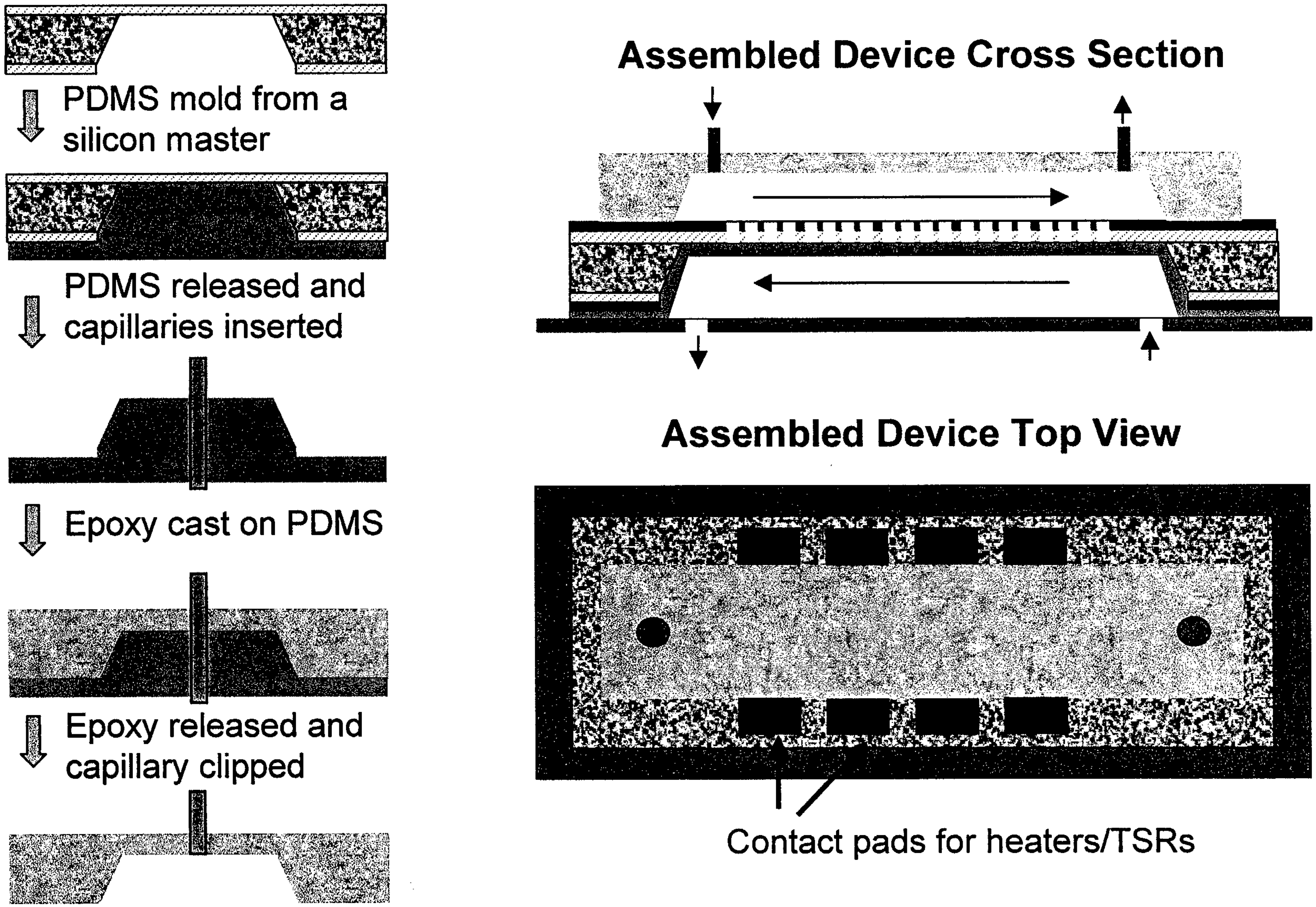


Opening of Pd membrane using BOE

Packaging using an aluminum plate on the bottom



Device Fabrication - Capping Channel



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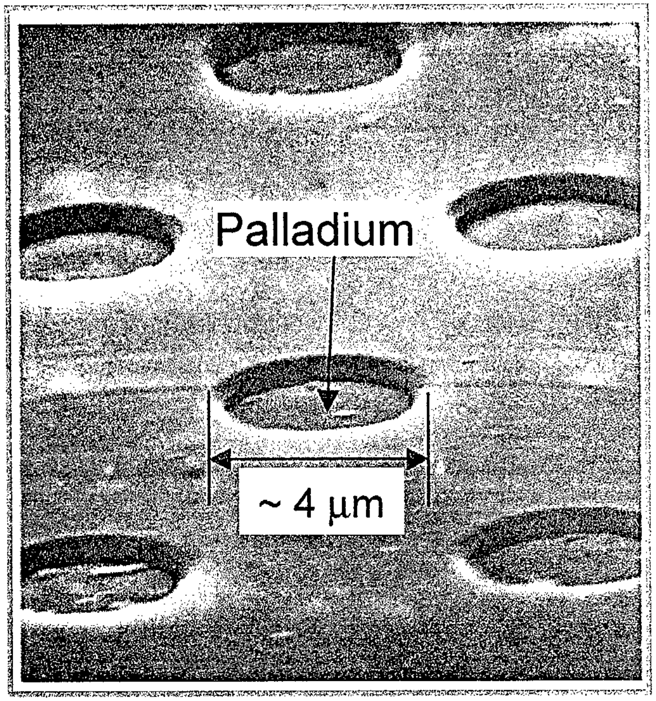
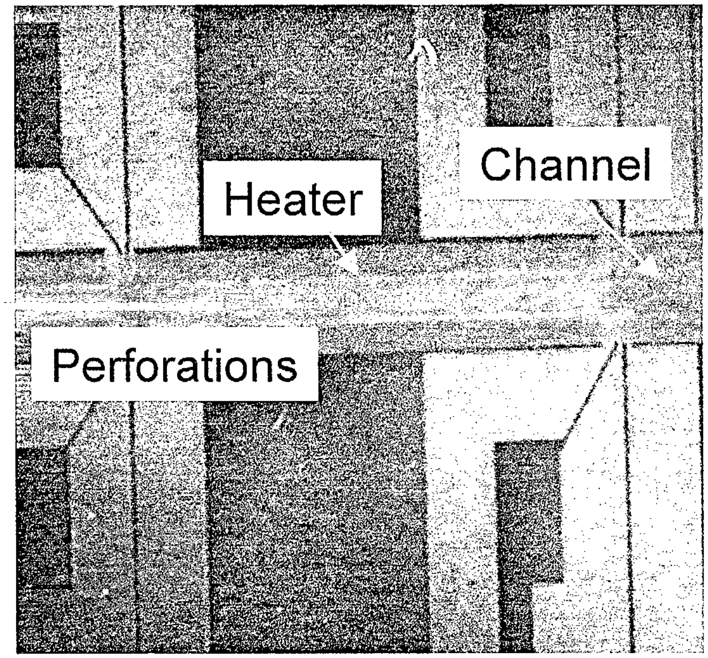
Microfabricated Pd Membranes





- Device dimensions:
  - Chip 0.8 x 1.6 cm
  - Channel 1.2 cm long (2-3 heater segments)
  - Membrane width ~ 700 μm
  - Perforation diameter ~ 4 μm

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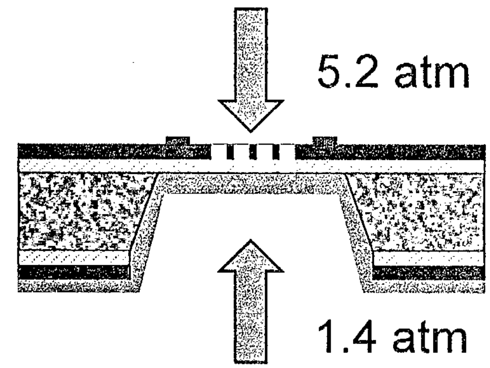
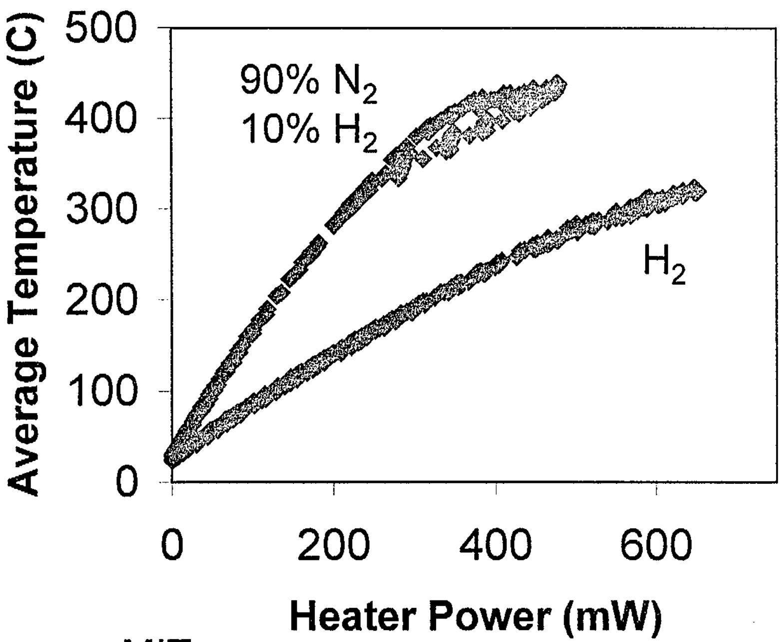
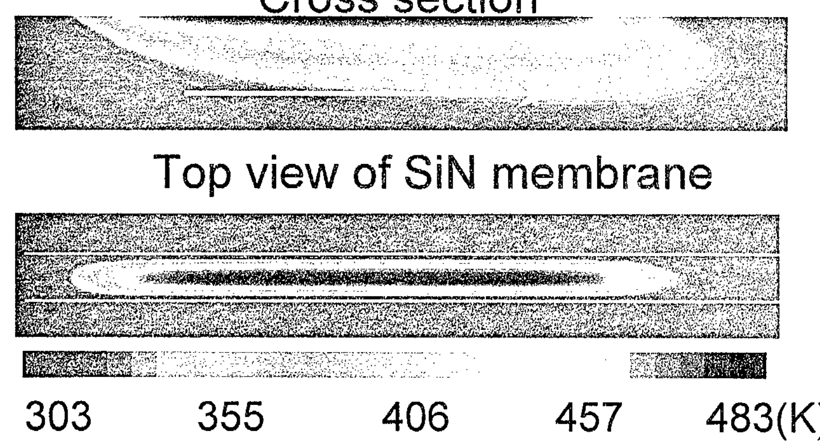
Device Heating and Structural Properties

- Thin membrane structure provides thermal isolation and efficient power utilization.
- The membrane is thermally compensated - no buckling at elevated temperatures.
- The membrane can withstand significant pressure gradients.
- Very fast thermal response time (~10 ms).

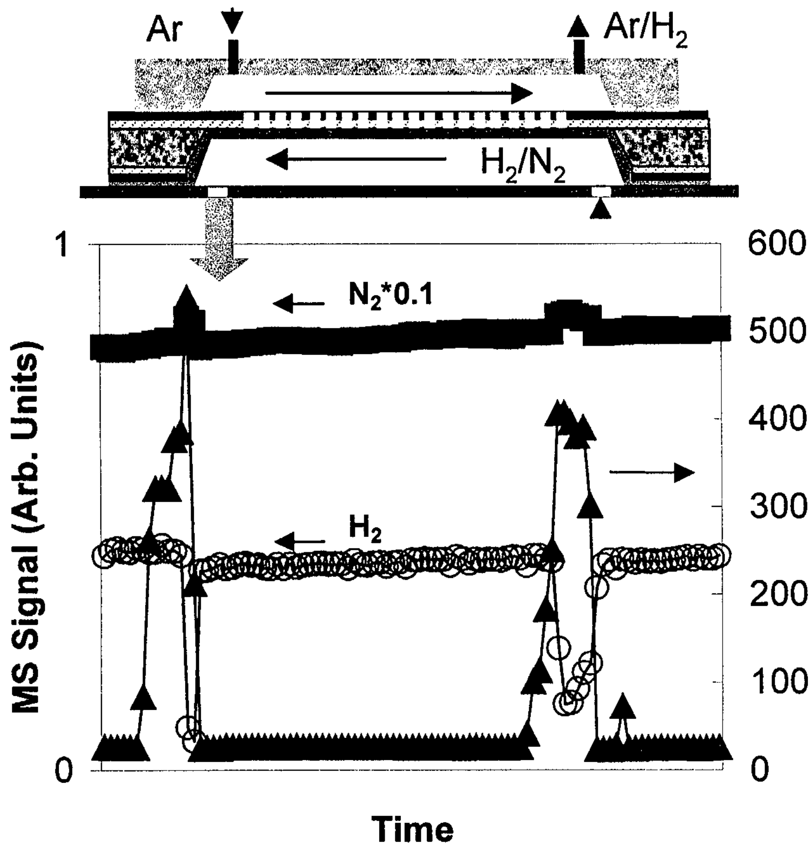


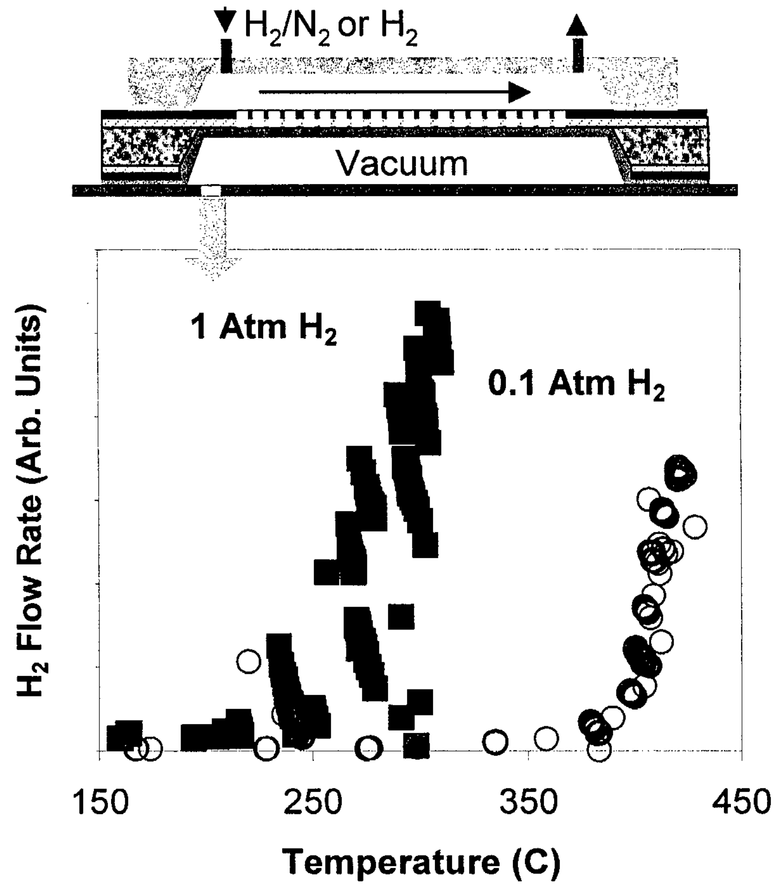




(I-M. Hsing, *et al.*, 1997)

Micromembrane Performance Characterization





- Selective flux of hydrogen achieved through Pd-micromembranes.
- Hydrogen flux dependence on temperature and pressure matches expectations.

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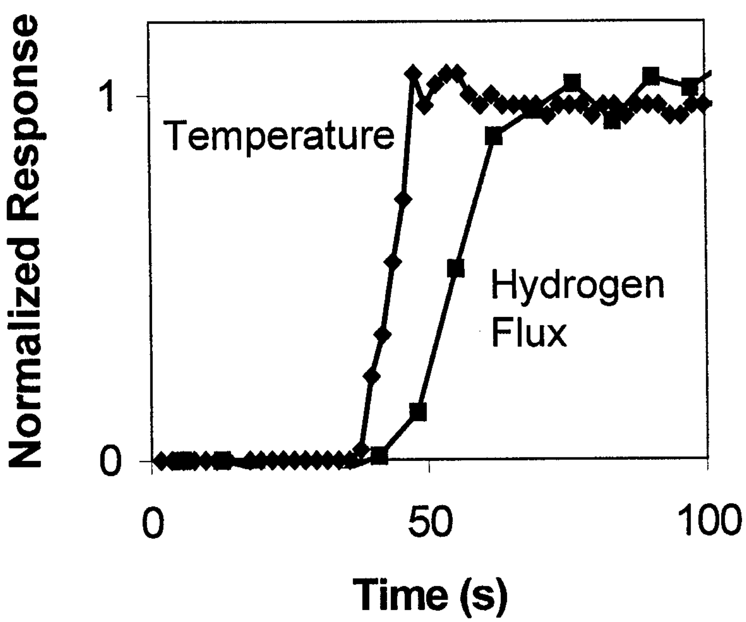
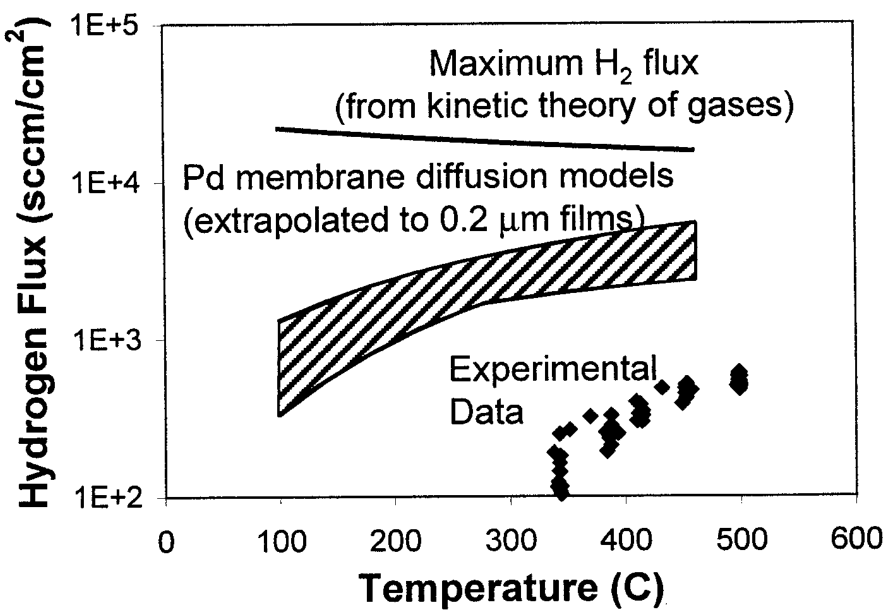
Device Response Time, Selectivity, and Flux





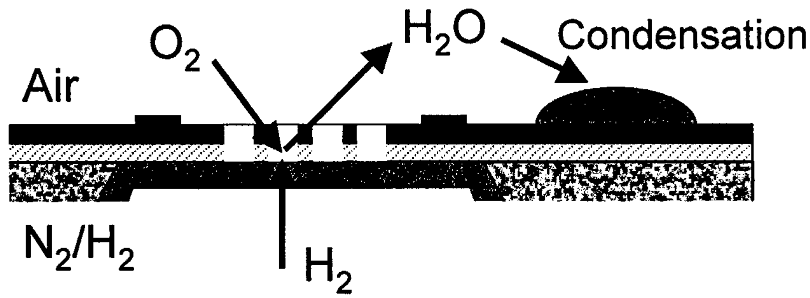
Measured S > 1800 !

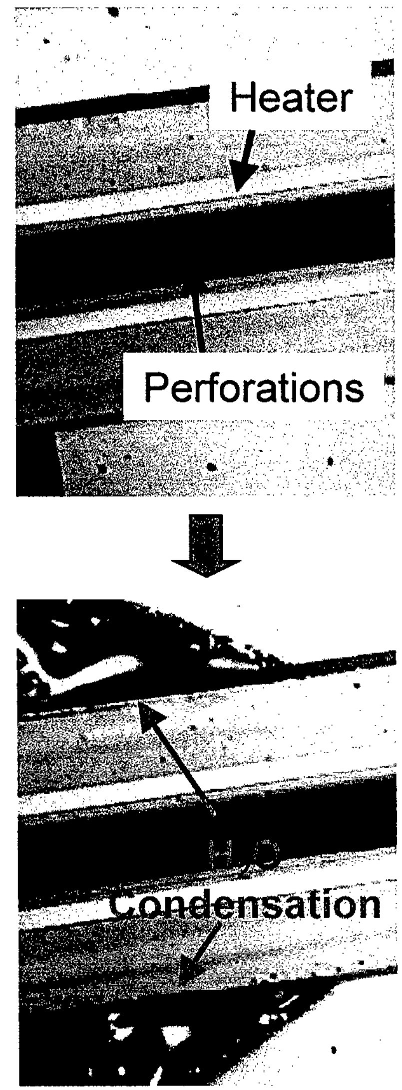
$$S = \frac{\left(P_{H_2} / P_{N_2} \right)_{Permeate}}{\left(P_{H_2} / P_{N_2} \right)_{Raffinate}}$$

- Very fast device response time (~10 s)
- Hydrogen flux diffusion limited
- Micromembrane selectivity very high (measurement limited)
- Very high hydrogen flux measured (~600 sccm/cm²)

Hydrogenation Reactions Using Pd Membranes

Experiment





- A model hydrogenation reaction demonstrated using the micro palladium membrane.
- Palladium membrane reactors offer advantages:
  - Beyond equilibrium conversions
  - Higher selectivity
  - Use of impure hydrogen feed streams
- Conventional technology limited by the high palladium cost for thick membrane films (10-30 μm).

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Microfabricated Gas Phase Reactor: Scale-Up & Packaging

K MIT

DARPA MicroFlumes

Reactor Components & Sub-systems Design

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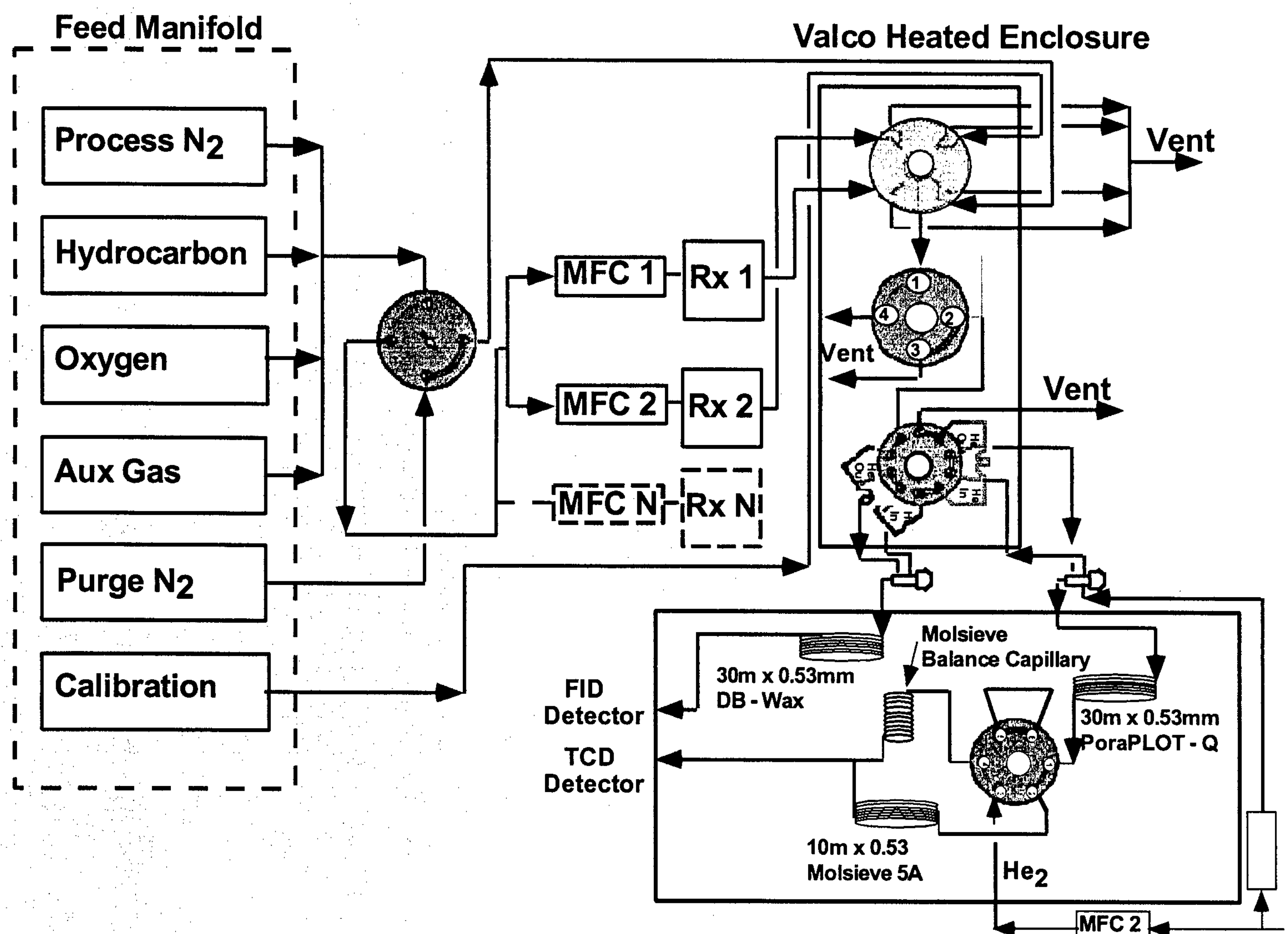
DARPA Gas Phase System Flow Schematic



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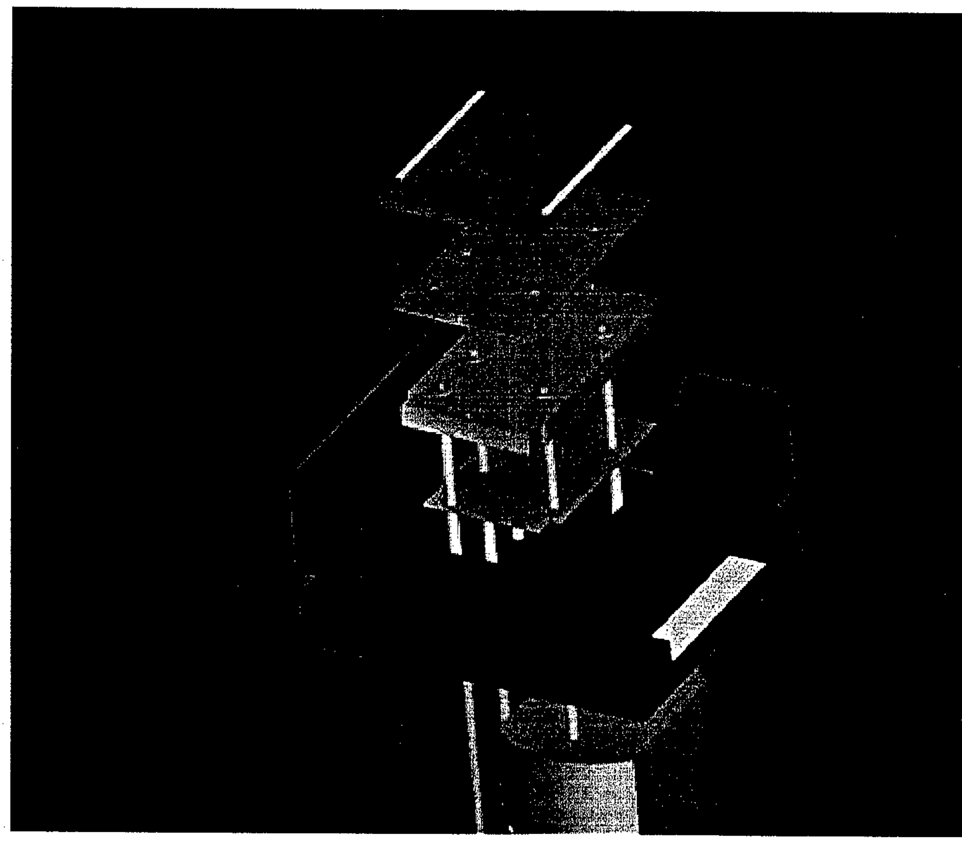
Reactor Mounting System



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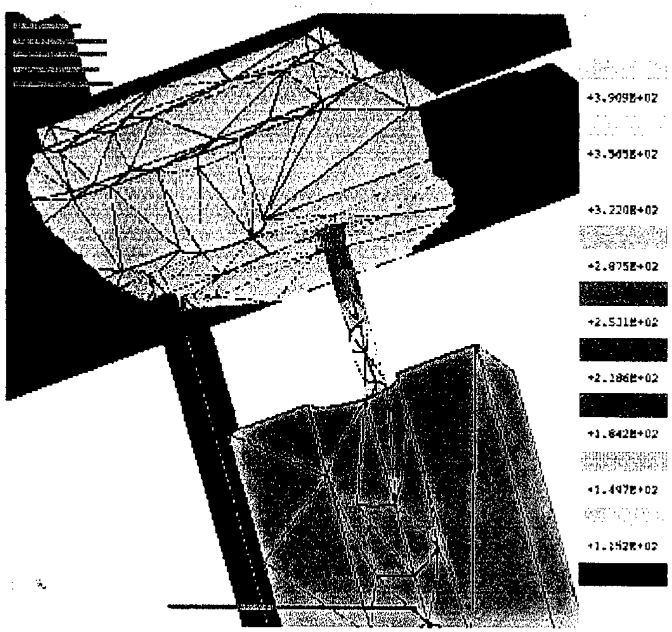
Picture

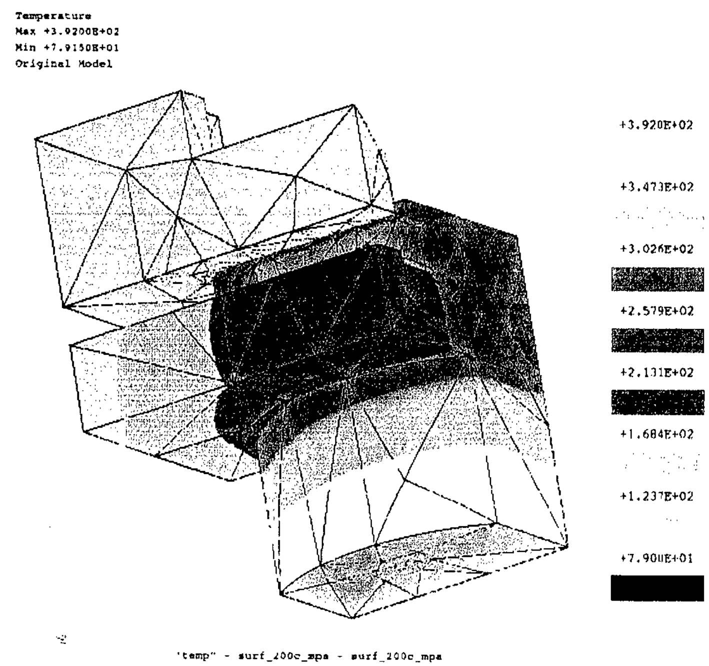
Reactor Card Assembly & Exploded View of The Reactor Components

Thermal Modeling

Without Radiation & Convection



With Radiation & Convection



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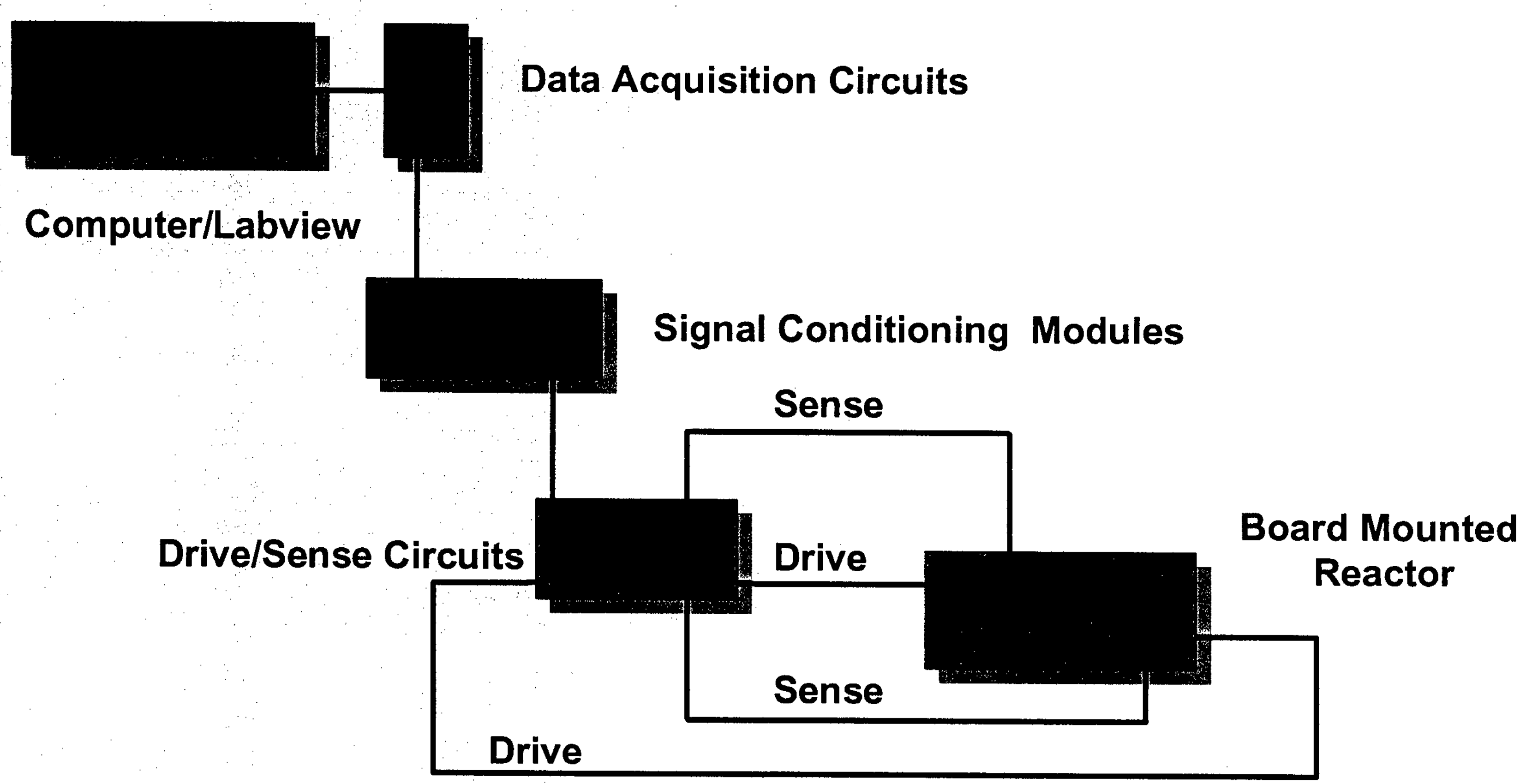
Electronic Components & Sub-systems Design

Control Circuit Block Diagram



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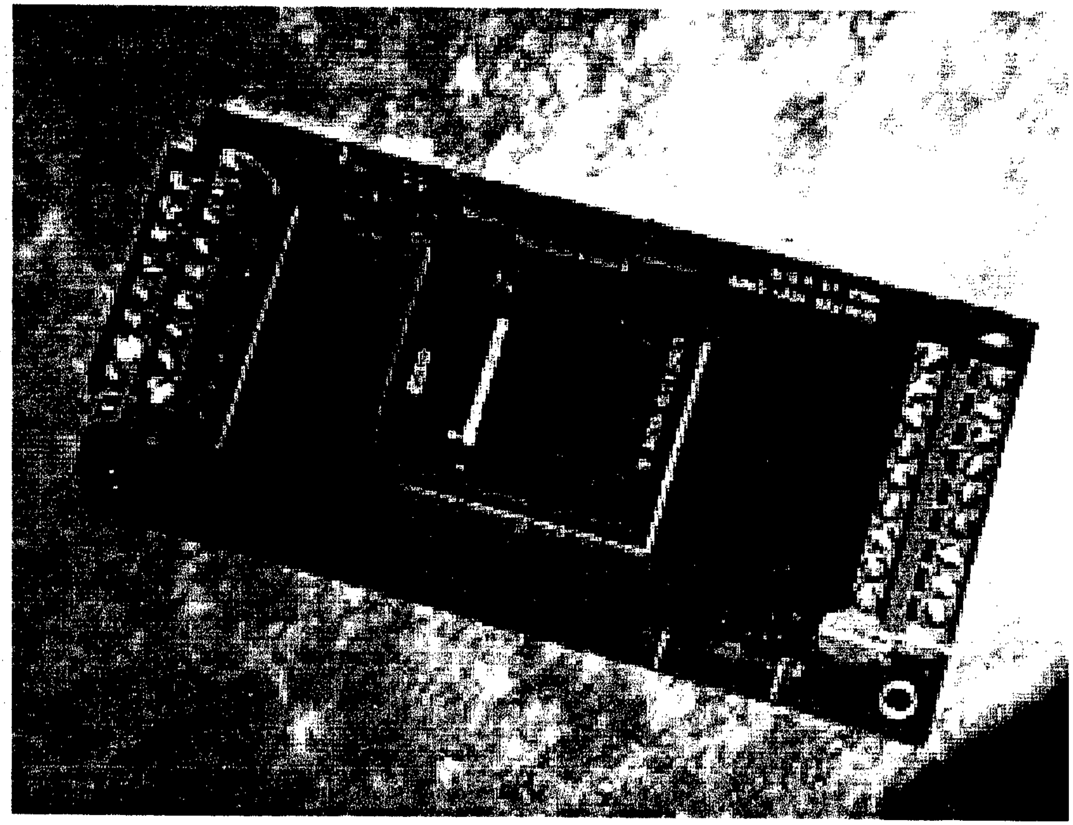
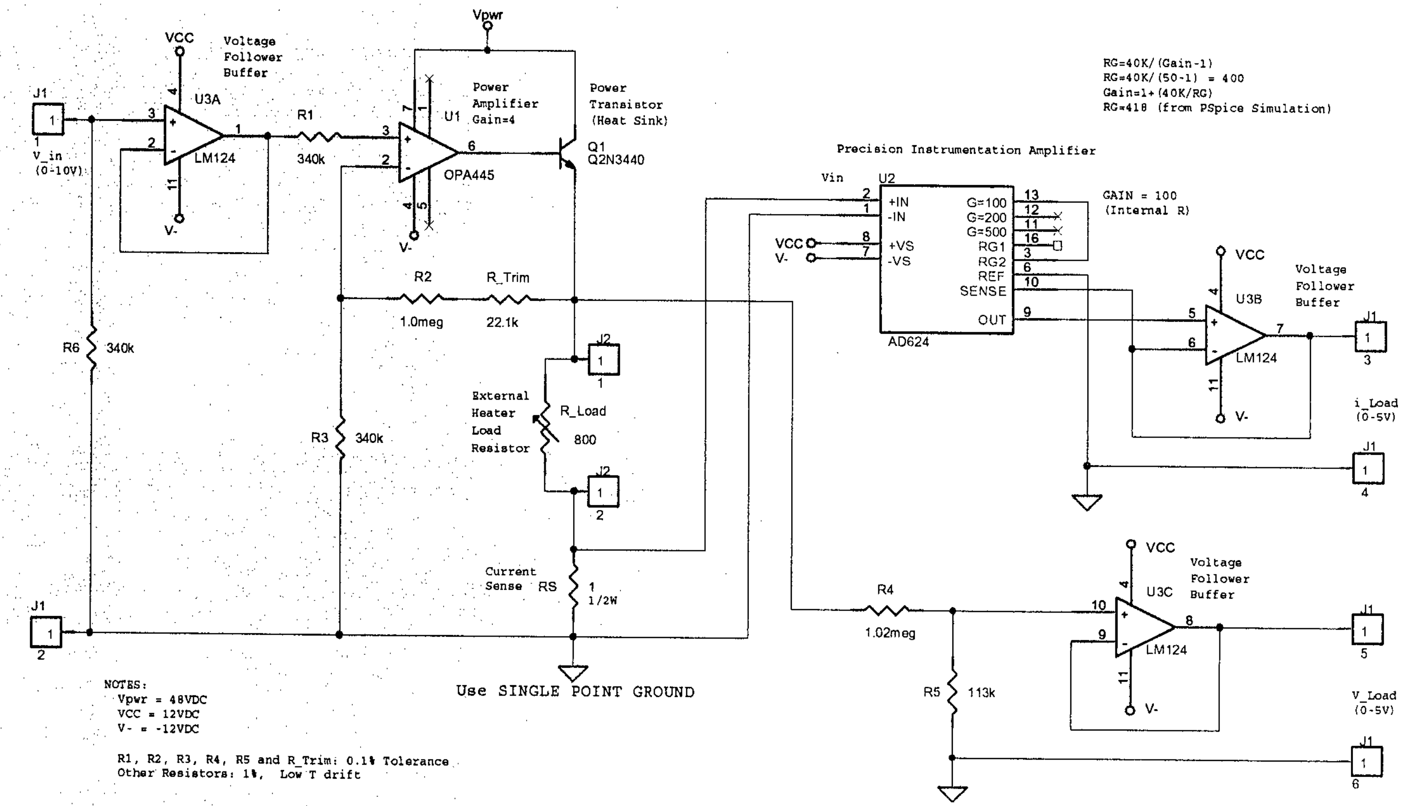
MultilayerPC Board With Diemate® Socket



Heater Drive Circuit

Heater Driver Circuit: Voltage-Controlled Amplifier with Voltage and Current Measurement
(Floating Load with 1.0 Ohm Current Sense Resistor to GND)



NOTES:
Vpwr = 48VDC
VCC = 12VDC
V- = -12VDC

R1, R2, R3, R4, R5 and R_Trim: 0.1% Tolerance
Other Resistors: 1%, Low T drift

Possible Low-cost Substitution: AD622 for AD624

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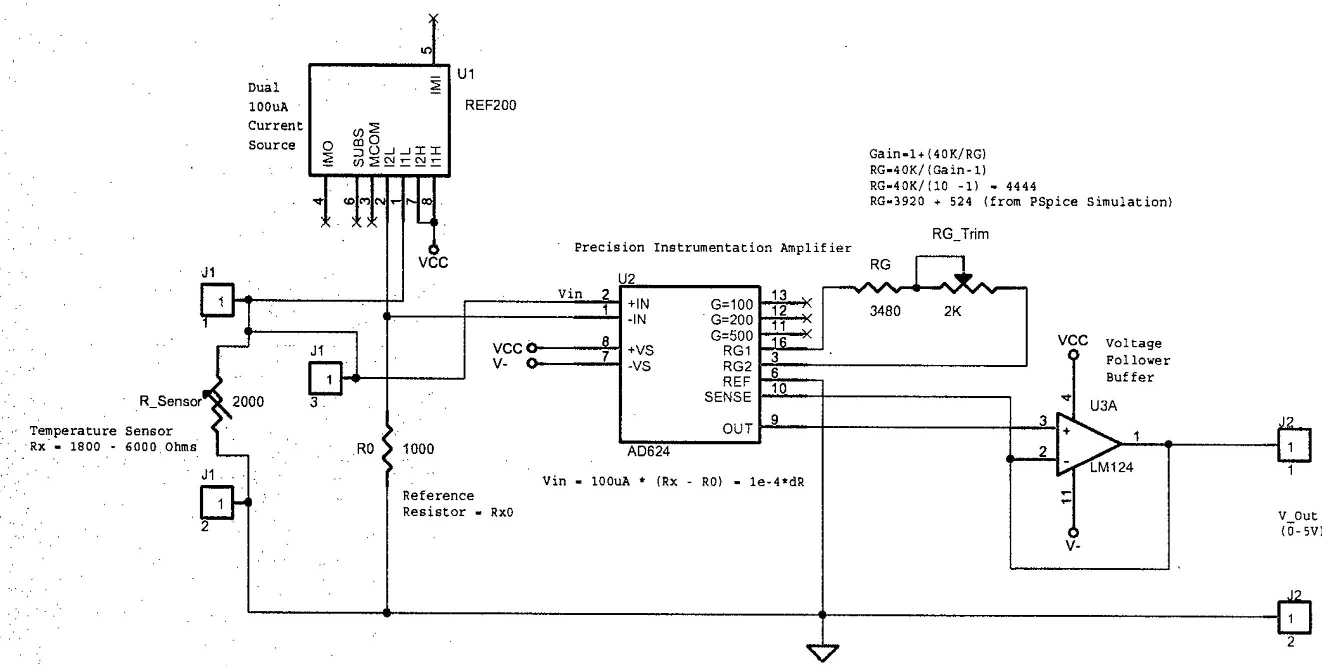
Temperature Measurements & Flo Sensing

Resistance Temperature Measurement: Temperature = f(R)



NOTES:
VCC = 12VDC
V- = -12VDC

Resistors R0 0.1% and RG 1%, Low T drift

Possible Low-cost Substitution: AD622 for AD624

Flow Sensing: RX = Downstream Resistor, R0 Upstream

R_Sensor Leads:
Use 4-Wire connection:
2 leads for excitation,
2 leads for sensing.

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MESOSCALE REFRIGERATOR

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Applications:

1. Thermal management in a hostile environment

In non-refrigerated cooling, no item can be cooled below the ambient (or heat sink) temperature. This system can provide cooling even in those cases, such as next to the engine block of a vehicle.

2. Refrigerated (and conditioned) suit

Temperature inside protective and other whole-body suits can reach a high value. System presented here can be used to make refrigerated suits.

Applications (cont.):

3. Distributed cooling

A number of miniature units can be used to replace a large system, and will provide several advantages:

- Distributed cooling as opposed to centralized cooling, thus eliminating duct losses.
- More freedom and choice in how and where we can install such miniature systems.

For example: If we have

36 *W*, 3 *inch* diameter miniature units, we need
100 of those units, and
0.5 *m* X 0.5 *m* surface area to provide
1 *ton* (3515 *W*) of cooling.

Motivation

1. PNNL
Vapor Absorption Refrigeration system being designed and fabricated by PNNL

2. MIT
Micro Gas Turbine system
Micro motor (face drive)

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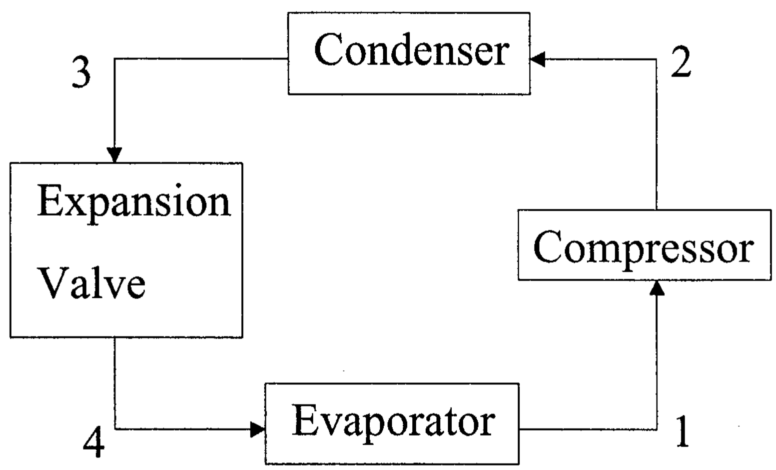
Comparison to Similar Systems

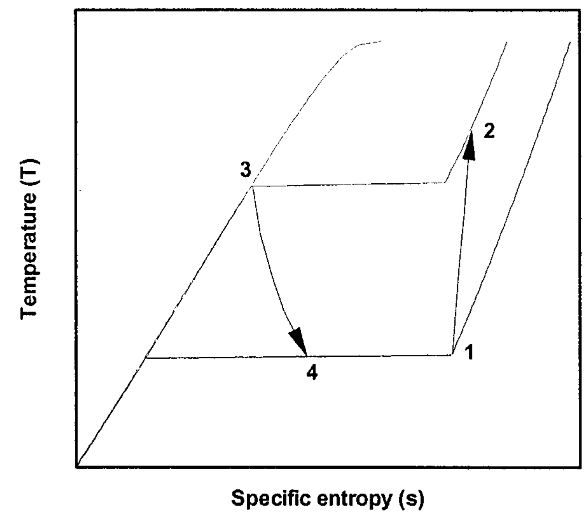
1. Vapor Absorption System of PNNL

- PNNL's design is less complex and easier to fabricate.
- The system presented here does not require any external heat source (desorption) and heat sink (for absorption) unlike the vapor absorption cycle.

2. Micro-engine and micro-motor of MIT

- Different system and application.
- MIT's design is more challenging.
- Compressor and motor designs for the system presented here have more modest specifications:
  - ➢ Lower RPM.
  - ➢ Lower temperature gradient across the system.





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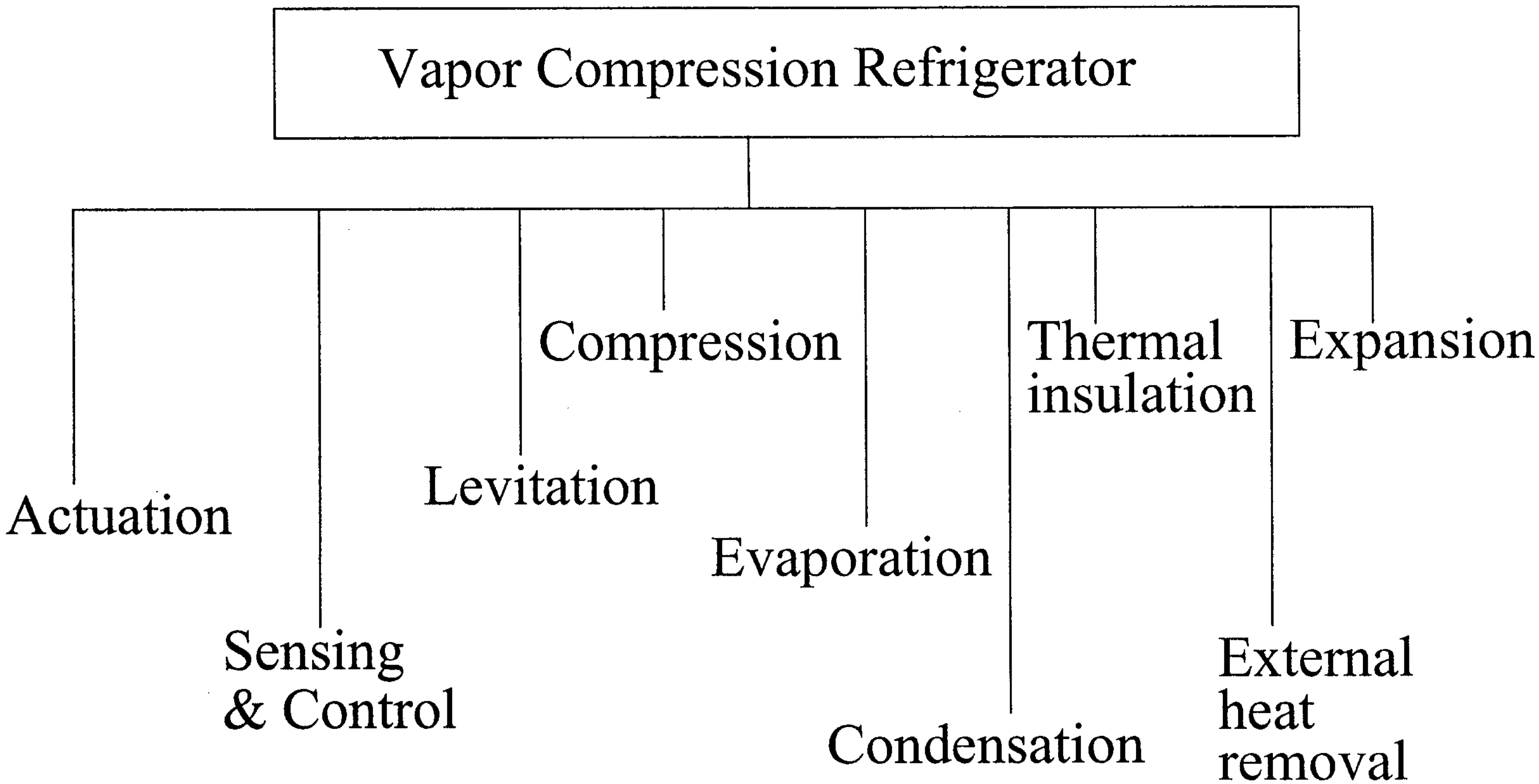
Design Specifications:

Refrigerant:	R134a
Evaporator Temperature T1:	$12^{o}C$
Ambient Temperature:	$45^{o}C$
Cooling Load:	$32W$
Outside Diameter:	$3\ inch(75mm)$

Overall Functional Decomposition



Design Alternatives Considered So Far

Actuator
- •Electromagnetic
- •Electrostatic
  - -VCM
  - -EIM
  - -Linear Comb Drive

Compressor
- •Centrifugal
- •Reciprocating
- •Sliding vane

Other items being considered:

Evaporator, integrated temperature (and heat flux) sensors, integrated quality sensors, fluidic controls.

Design Alternatives Considered So Far

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Compressor
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- •Reciprocating
- •Sliding vane

Other items being considered:

Evaporator, integrated temperature (and heat flux) sensors, integrated quality sensors, fluidic controls.

Current Status:

- Evaporator

  Preliminary design has been completed. Fabrication steps have been outlined. Masks are being prepared. Test setups (which are not necessarily miniature items) are being designed/fabricated.

- Compressor

  Centrifugal

  Preliminary design being completed. Fabrication process for a model will start soon.

  Reciprocating: Preliminary design started.

- Actuator

  VCM:

  Preliminary design completed. Fabrication steps have been outlined. Masks are being prepared.

  EIM, Linear Comb Drive: Preliminary design started.

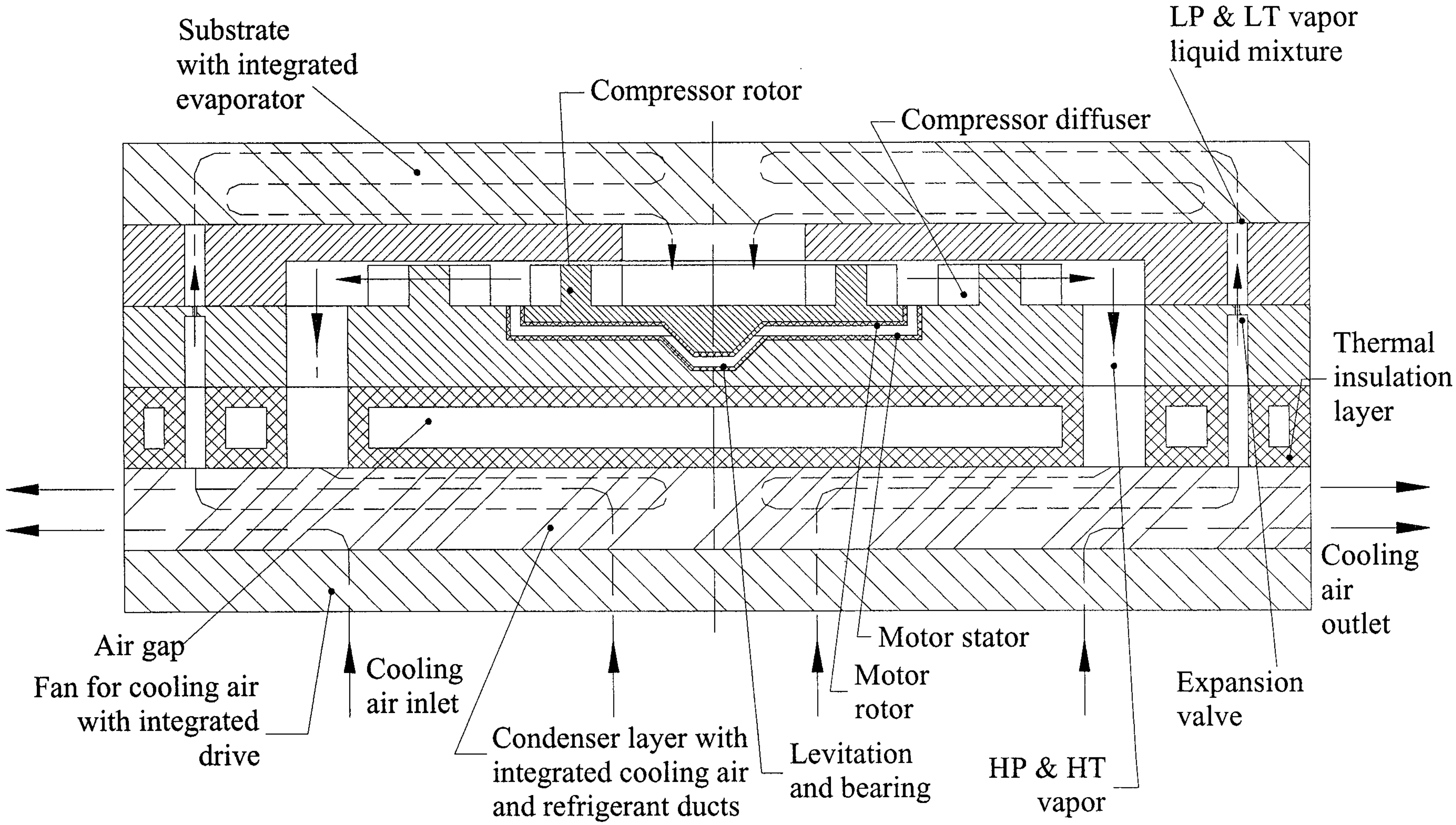
Design Details: Some Examples

(with Centrifugal compressor and VCM actuator combination)

Compressor power:	9.57
Compressor pressure ratio:	3.80
COP:	3.34
Impreller & rotor OD:	1.2 *cm*
Rotational speed:	400000 (approx.)
Motor excitation voltage:	620 V
Number of phases:	3
Number of rotor pads:	100
Number of stator pads:	150

An Overall Schematic

(with Centrifugal compressor and VCM actuator combination)



Forthcoming Publications

DESIGN AND ANALYSIS OF A MESO-SCALE REFRIGERATOR

N. S. Ashraf, H. C. Carter III, K. Casey, L. C. Chow, S. Corban, M. K. Drost, A. J. Gumm, Z. Hao, A. Q. Hasan, J. S. Kapat, L. Kramer, M. Newton, K. B. Sundaram, J. Vaidya, C. C. Wong, K. Yerkes

To be presented at session on "Microscale and Mesoscale Energy Systems" at the 1999 International Mechanical Engineering Congress and Exposition in Nashville, November 14-19, 1999.

COMPONENT FABRICATION AND TESTING FOR A MESO-SCALE REFRIGERATOR

N.S. Ashraf, L. C. Chow, A. Q. Hasan, J. S. Kapat, K. B. Sundaram, J. Vaidya

AIAA 1999 Space Technology Conference and Exposition in Albuquerque, September 28-30, 1999.

CFD Research Corporation

215 Wynn Dr., Huntsville, AL 35805 (256) 726-4800 FAX: (256) 726-4806 www.cfdrc.com

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COMPUTATIONAL DESIGN TOOLS FOR MICROCHEMICAL SYSTEMS

by

A. Krishnan, S. Krishnamoorthy, and M. G. Giridharan

CFD Research Corp.

Huntsville, AL 35805

Poster Presented at

Workshop on Microchemical Systems

and their Applications

June 16-18, 1999

Reston, VA

PR-99-28/1

CFD DESIGN TOOL

Abstract

A Modeling and Simulation Tool has been Developed to Aid the Design of Microchemical Systems.

Equations for Fluid Flow, Heat Transfer, Chemistry, Electrostatics, and Electrochemistry are Solved Implicitly in a Coupled Fashion to Achieve High Accuracy and Fast Convergence. The capabilities of this Tool are Demonstrated for a Microreactor, a Microcombustor, a Micro-Fuel Cell and a Meso-scale Heat Exchanger.

CFD-ACE+ Features

- Implicit, Pressure-based Finite-Volume Approach
- k-ε, RNG k- ε, low Re Turbulence Models
- Fast, Equilibrium and Finite-Rate Chemistry Options
- Multi-step, Homogeneous and Hetrogeneous Chemistry
- Link with CHEMKIN
- Coupling with Electrostatics, Structural Analysis, Electro-kinetics
- Structured, Unstructured and Hybrid Meshes
- Interfaces with CAD Packages
- User-Friendly Graphical User Interfaces

PR-99-28/2

MIT/DUPONT T-REACTOR

- High Surface Area/Volume Ratio
- Prevent Runaway Reactions
- Point-of-Use Generation
- Scale-Up
- Partial Oxidation of Ammonia

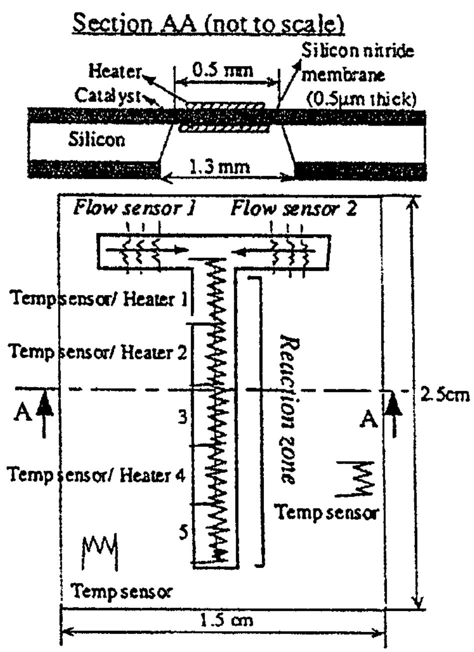
Ammonia Oxidation Mechanism (Pignet and Schmidt, 1975)

$NH_3 + 5/4\ O_2 \rightarrow NO + 3/2\ H_2O$

$NH_3 + 3/2\ NO \rightarrow 5/4\ N_2 + 3/2\ H_2O$

$NH_3 \rightarrow 1/2\ N_2 + 3/2\ H_2$

MIT/DuPont Reactor Configuration



CFD Model

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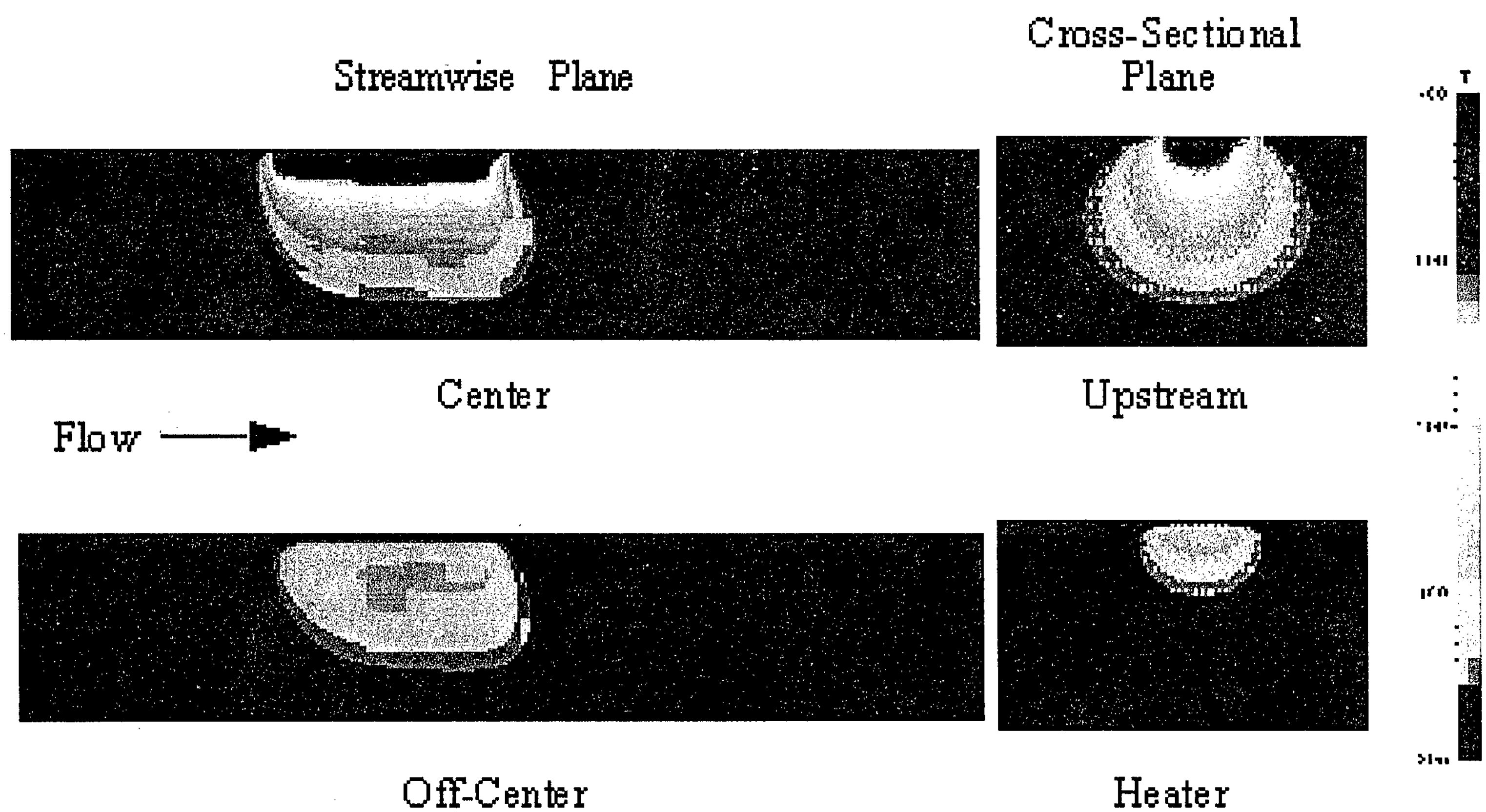
PR-99-28/3

MIT/DUPONT T-REACTOR (CONT'D)

CFD-ACE+ TEMPERATURE PREDICTIONS



PR-99-28/4

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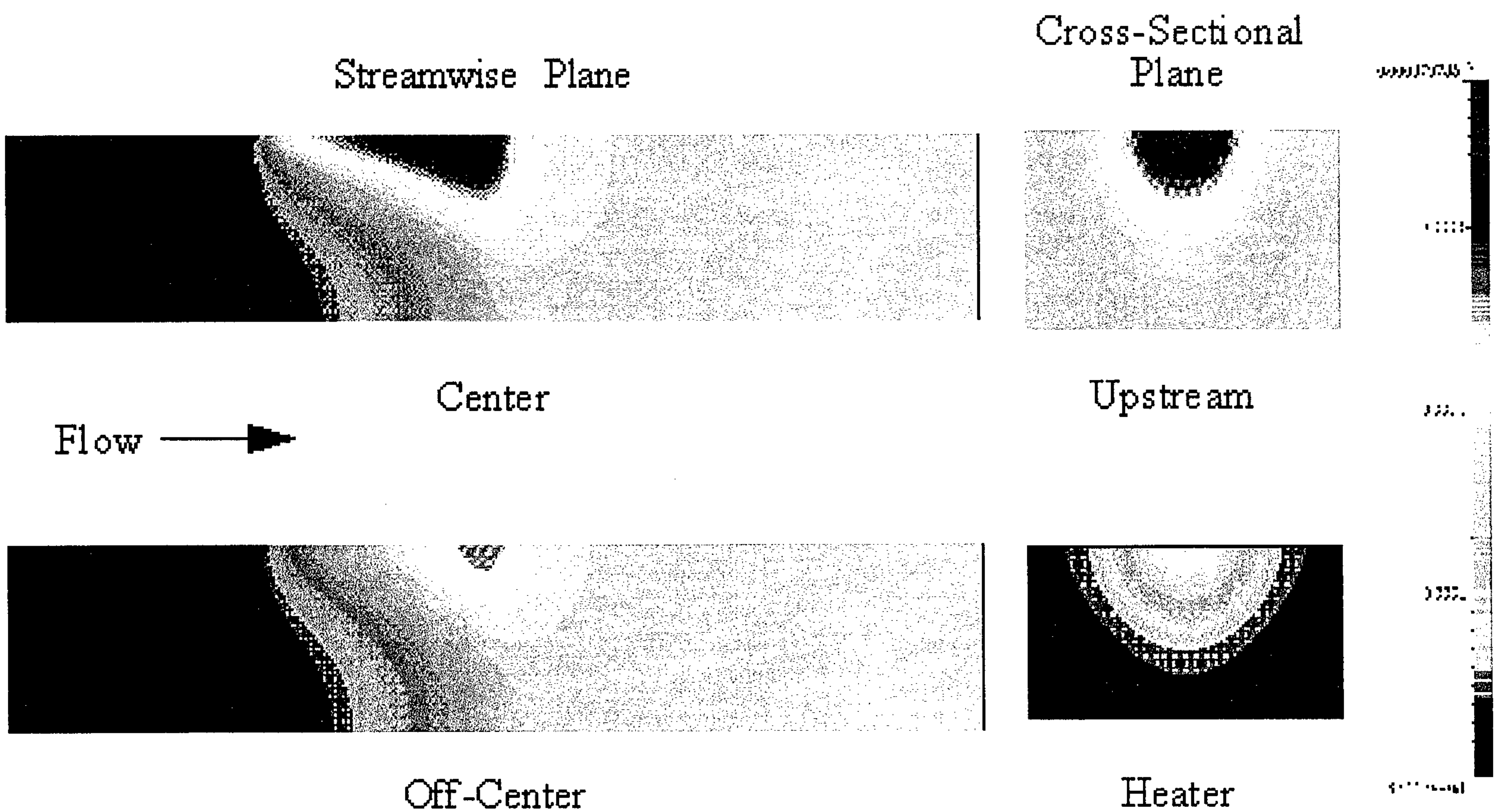
MIT/DUPONT T-REACTOR (CONT'D)

CFD-ACE+ NO MASS FRACTION DISTRIBUTION



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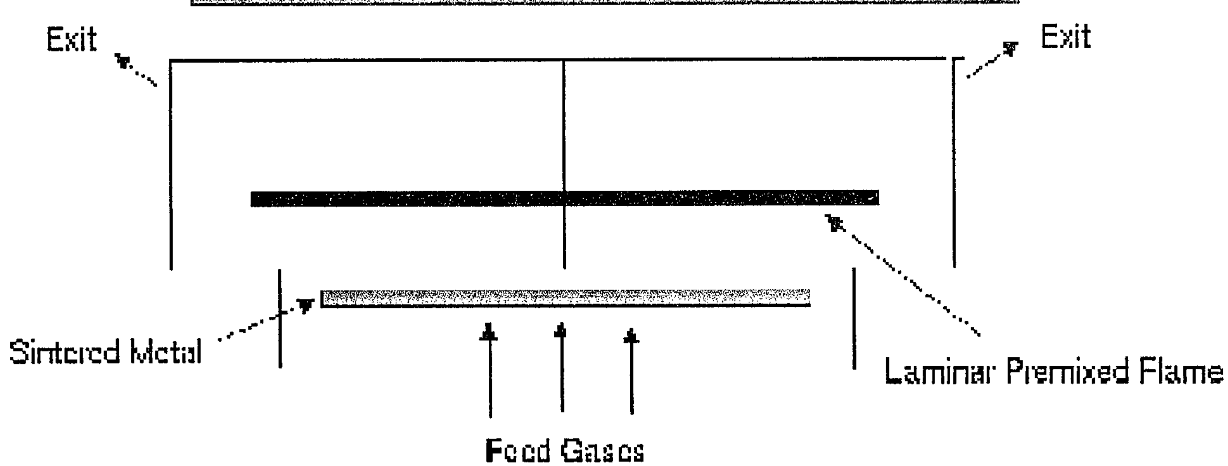
PR-99-28/5

BATTELLE MICROCHANNEL COMBUSTOR/EVAPORATOR

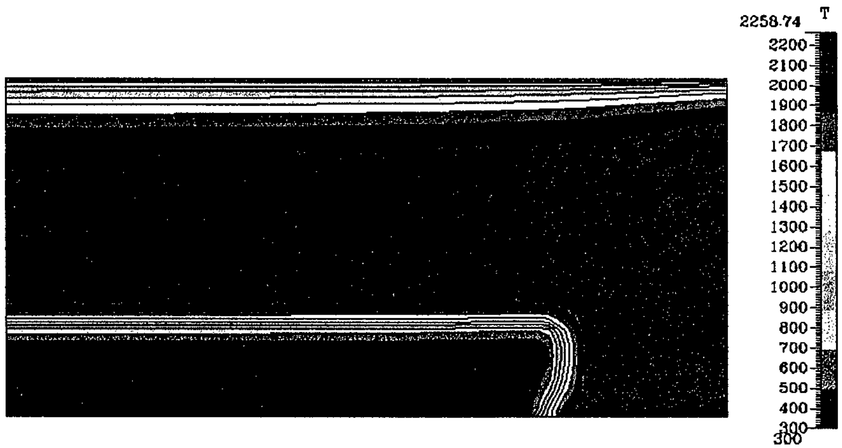
- Lightweight Compact Power Source for Soldier Heating and Cooling Systems
- Hydrocarbon Fuels Provide High Energy Density
- Methane Fuel
- Equilibrium Chemistry
- Emission Predictions

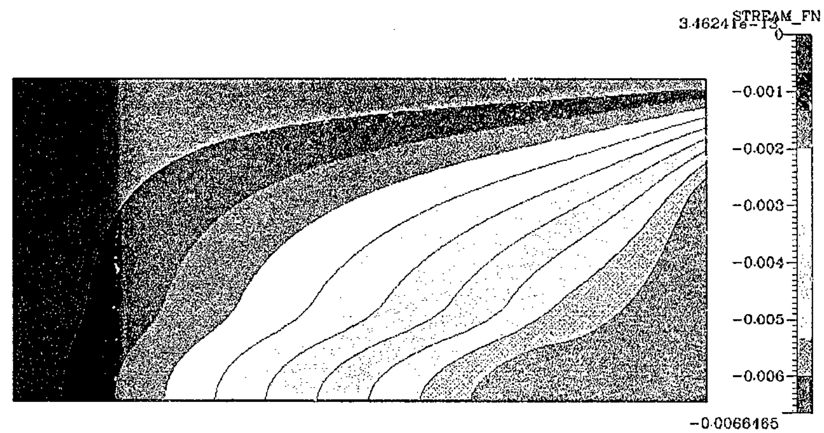
Battelle Integrated Combustor/ Evaporator Configuration



INTEGRATED MICROCHANNEL COMBUSTOR/EVAPORATOR

CFD-ACE+ Temperature and Streamline Predictions





Comparison of Emission Predictions with Data

	NOx (ppm)	CO (ppm)
California South Coast Area Small Boiler Emission Limits	< 30	< 400
Battelle (PNNL) Microcombustor Data	19	16600
CFD-ACE Predictions	27	8836

PR-99-28/7

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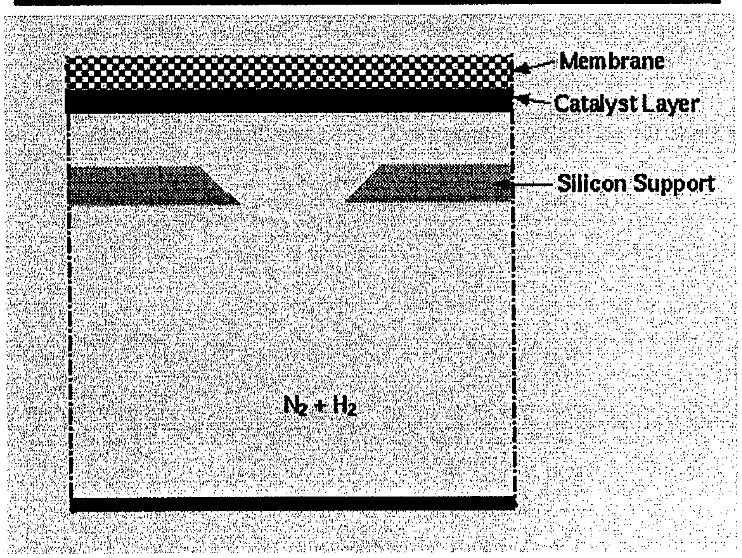
MICRO-FUEL CELL

- Environmentally Acceptable Power Source
- Inter-atomic Bond Energy Directly Converted to Electrical Energy
- Absence of Moving Parts
- Scale-Up

Physical Phenomena

- Species Transport
- Charge Conservation
- Electrochemistry
- Multi-component Diffusion
- Multi-phase Flow and Heat Transfer

Micro-Fuel Cell Configuration



Hydrogen Mass Fraction Distribution

PR-99-28/8

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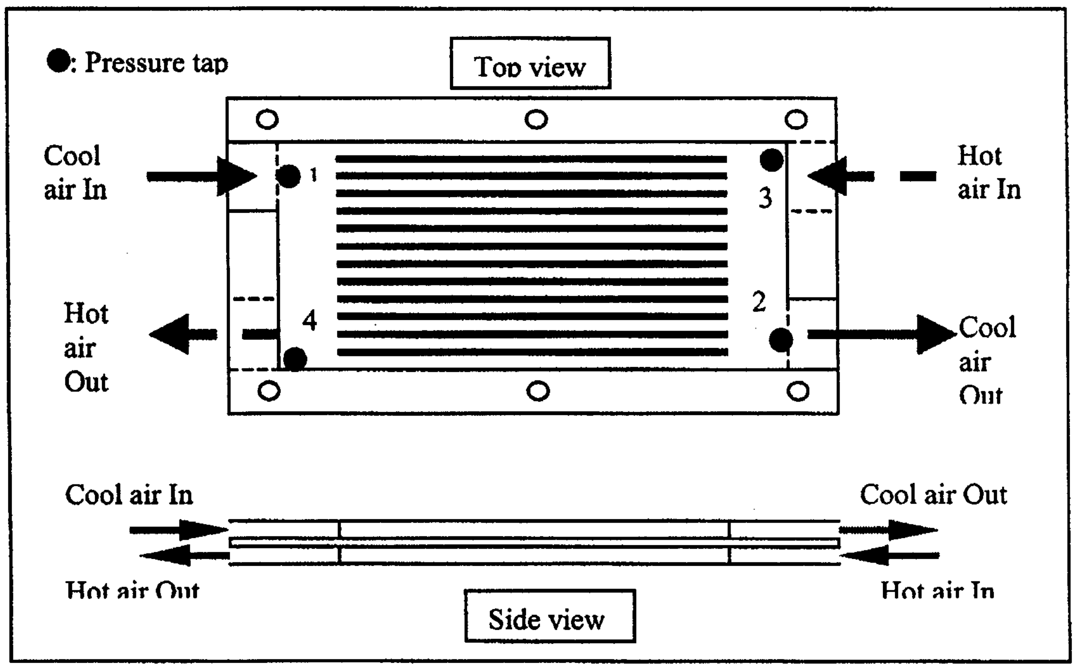
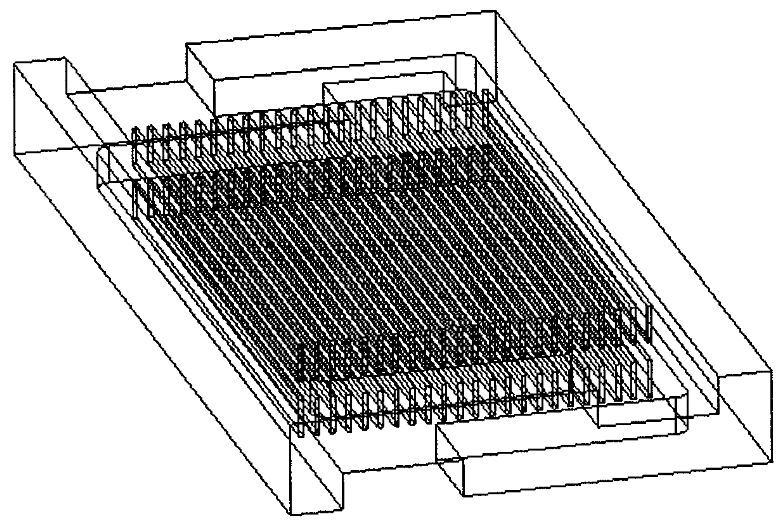
MESO-SCALE HEAT EXCHANGER

- Developed by Meso-scale Systems Technologies, Inc.
- Thermo-Catalytic Systems for Air Purification
- Stacked Counter-flow Heat Exchangers

Meso-scale Heat Exchanger Configuration



CFD Model



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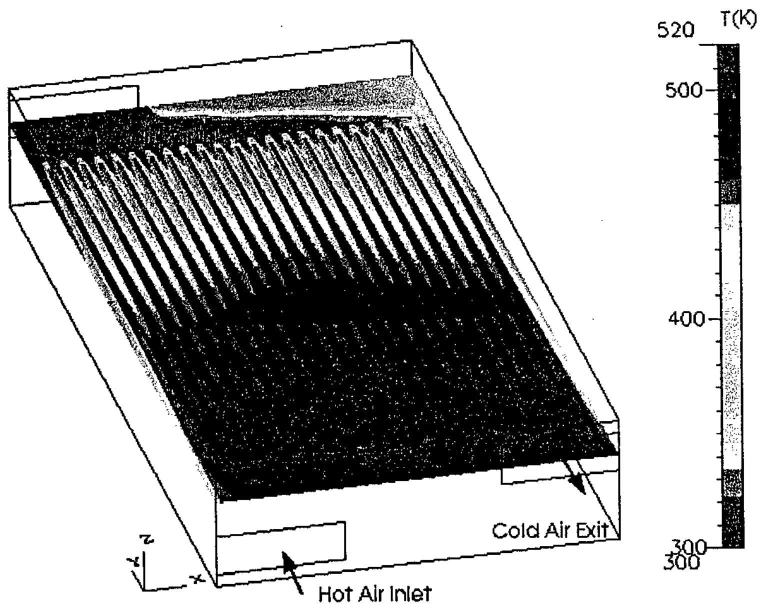
PR-99-28/9

MESO-SCALE HEAT EXCHANGER (CONT'D)

CFD-ACE+ PREDICTIONS

Temperature Distribution



Pressure Distribution

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OPPORTUNITIES FOR MICROENERGY DEVICES

Working Group

Robert Wegeng - PNNL (Leader)

Workshop on Microchemical Systems and their Applications

June 16-18, 1999

784

MicroenergyDevices Working Group

- Objectives
  - Identify application areas
  - Identify critical scientific and engineering problems
  - Identify opportunities for research and development

- Products
  - Short summary of the working group discussion
  - Report (to be included with the workshop proceedings)

MicroenergyDevices Working Group

- Including…
  - Fuel processing (partial oxidation, hydroforming, catalysts)
  - Exhaust conditioning
  - Converter technology (TPV, TE, fuel cells, microturbines)
  - Microfluidics (pumps, valves, integration)
  - Energy Integration
  - Systems Integration and Packaging

7-56

MicroenergyDevices Working Group

Group Process

- Identified issues associated with development and operation of microchemical systems
- Presentation on soldier power from Scott Feldman (Soldier Systems Command)
- Brainstorming
  - Identified applications
  - Selected two applications with high value
  - Identified how microchemical systems can provide unique performance advantages
  - Identified methods (e.g., soldier power production using microreformers and fuel cells)
  - Identified scientific and engineering challenges/needs

MicroenergyDevices Working Group

Application/Product Issues

- Applications
- Figures of merit
  - Power, energy density, power density, weight, costs, durability, lifetime, mean time between failures, endurance, environmental disposal issues
- Other end-use product requirements and how each fits into a system
  - Signature (for stealth applications): Thermal, em waves, noise, exhaust, other inputs and outputs
  - Range of conditions (applicability across)
  - Transients: Startup, shutdown, cycling, transients, instabilities
  - Turndown requirements

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Uniqueness Issues

- What is unique? i.e., What can these technologies do that other technologies cannot do? What is the compelling arguments/applications that drive investments?
- Large surface/volume ratio... high pressures... how will these limit or enhance performance?
- Heat and mass transfer rates
- Effect of short residence times -->Nonequilibrium products (example)

MicroenergyDevices Working Group

Size/Scale Issues

- What are the scaling rules?
- What is the best size for an application?
- Scaling up vs numbering up
- How does scale affect physics, chemistry, engineering?

MicroenergyDevices Working Group

Systems Issues

- Tradeoffs to gain system performance (e.g., singleversus hybrid technologies
- Need for new diagnostics
- Understanding of operating characteristics of components, systems (e.g., lack of a Microchemical Systems Engineering Handbook)
- Standard approach to modeling may be the wrong approach (e.g., equilibrium sometimes not obtained)
- Current engineering "knowledge/instinct" not necessarily accurate at microscale

MicroenergyDevices Working Group

Systems Issues (continued)

- Interfacing with the macro world
- Pressure drops, parasitic losses, system design for…
- Selection of materials and fabrication methods for a given product
- Thermal insulation/management for small power systems (e.g., reactors)
- Closed systems versus open systems (e.g., underwater power generation, where oxidizers might be required)

MicroenergyDevices Working Group

Power Generation Issues

- What is the appropriate fuel?
- Fuels constituents (e.g, levels of sulfur and other catalyst poisons)
- Air impurities (effects of)
- May have to use low-sulfur fuels, solid oxide fuel cells...

MicroenergyDevices Working Group
Other Specific Issues

- Microfluidics
  - Fouling of microchannels; deposition on surfaces
  - Multiphase flow and other flow distribution issues (potential for flow maldistribution), manifolding, system degradation
- Catalysts not developed/optimized
  - How do you put catalysts in?
  - Systematic approach to identifying appropriate catalysts
  - Fast reactions
  - High conversions
- Sorbents (generally ditto to above)
  - Desorption, engineering for...

MicroenergyDevices Working Group

Applications

- Low Power, Long Duration Systems (>1 hour)
  - Soldier power
  - Power for remote systems
  - Power for stationary rechargers
  - Cogen systems for camp power
  - Robotic power (air, ground, undersea)
  - Small arms (guided munitions)
  - Distributed sensing
  - Backup power
  - "Still Suits" aka Dune by Frank Herbert
- Heating and Cooling
  - Soldier Cooling

MicroenergyDevices Working Group
Soldier Power

- Soldier Power State-of-the-Art
  - Daypack battery
  - 3.5"x 3.5"x 7.0"
  - 4 lb.
  - 560 Wh

MicroenergyDevices Working Group
Soldier Power

- Functional Requirements for Soldier Power
  - 10-40 We
  - 1 - few kg system
  - 400 watt-hours or better
  - Logistics or clean fuels
  - 3-day to 12-day operation
  - -40 to -120 F
  - low emissions
  - Insignificant thermal signature for some applications

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MicroenergyDevices Working Group

Unique Value fromMicrochemicalSystems

- Soldier Power
  - Rapid heat and mass transport at small scale can potentially produce:
    - High power density heat exchangers
    - High power density combustors and chemical reactors (when kinetics are fast)
    - Cooling for fuel cells
  - Micro/meso fabrication methods can potentially produce ultra compact turbomachinery and associated peripherals (e.g. pumps, valves, fans, filtration, etc)
  - Potential for fuel processor/combustor and energy converter to be very small compared to the size of the fuel that a soldier has to carry at any time (i.e., the energy density of the total system including fuel is essentially the same as the energy density of the fuel)

MicroenergyDevices Working Group
Soldier Power

- Representative microscale solutions
  - Reformer/fuel cell
  - Combustion/TE, TPV, and alternative thermal cycles
  - Capacitor/Battery
  - Turbomachinery

MicroenergyDevices Working Group
Soldier Power - R&D Needs

- Reformer/Fuel Cell
  - Reacting & non-reacting fluid mechanics & simulation
  - Micro/meso fabrication with high temp. materials
  - Sulfur management
  - Low temperature ion conducting as solid electrolyte for fuel cells
  - More active oxygen reduction catalysts at cathode
  - Higher power density fuel cells
  - Associated components (pumps, valves, fans, control elements)

MicroenergyDevices Working Group
Soldier Power - R&D Needs

- Combustion & TE/TPV R&D Needs/Challenges
  - Integral controls (actuators, valves, sensors…)
  - Pollution control (most importantly: CO)
  - Materials for combustion walls
  - Thermal insulation
- Multiple solutions to problem…
  - Homogeneous/Heterogeneous combustion
  - Liquid hydrocarbons or alcohols

MicroenergyDevices Working Group

Man Portable Cooling

- Man Portable Cooling State-of-the-Art
  - Cooling vest
  - 150 W cooling
  - 10 lb.

MicroenergyDevices Working Group

Man Portable Cooling

- Functional Requirements for Man Portable Cooling
  - 300 - 400 W
  - 5 - 7 lb.
  - Could provide electricity in addition to cooling...

MicroenergyDevices Working Group

Unique Value fromMicrochemicalSystems

- Soldier Cooling
  - Both vapor-compression and absorption cycle systems are candidates.
  - Micro/meso fabrication methods can potentially produce ultra compact turbomachinery (i.e., compressors) and associated peripherals (e.g. pumps, valves, fans, filtration, etc)
  - Rapid heat and mass transport at small scale can potentially produce:
    - High power density heat exchangers
    - High power absorbers and desorbers
    - High power density combustors
  - Radiator is a limiting component (air-side heat transfer)
  - Potential for reductions in overall weight burden for soldier through integration of cooling system with other hardware (e.g., with power generation units)

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MicroenergyDevices Working Group

Soldier Cooling -- R & D Needs

- Detailed Modeling and Diagnostics
  - Reacting and nonreacting fluid mechanics in microstructures (especially wrt boundary conditions)
  - Two-phase flow for microporous contactors
- Radiator
  - To reduce radiator volume/weight: Heat transfer enhancement through active or passive microstructures

8035

MicroenergyDevices Working Group

Conclusions - I

- Highest value applications
  - Soldier power
  - Soldier cooling
- Crosscutting needs:
  - Peripherals (pumps, valves, fans, filtration, controls)
  - High temperature materials
  - Micro/meso fabrication methods
  - Insulation requirements

MicroenergyDevices Working Group
Conclusions - II

- The best fuel for soldier power may not be the best fuel for a tank…
  - Sulfur in logistics fuel may cause added process hardware for fuel processor
  - Methanol (or other fuels) may be a better solution to thermal integration/management issues (multiple reactors with potentially different temperature requirements)
- Airside heat transfer enhancements really important for soldier cooling
- We need a fundamental and basic understanding of the operational characteristics of microchemical components and systems

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Working Group II: Challenges and Needs in Microfabrication and Materials

~ 9 Quality People

How we organized

- Agreed to start at 9AM
  - Fewer people - fewer fights - less time
- Agenda
  - What are the applications (30 minutes)
  - Benchmark materials and technologies (1 hr)
  - Identify needs (1 hr)
  - Discuss (45 minutes)
    - Infrastructure / Standards / Modeling
    - Packaging, Integrated vs. Hybrid

Applications

- Power Generation / Energy Conversion
- Analysis
  - MicroTAS
  - Screening
- Environmental
- Synthesis
- BioMEMS

Issues to Consider

- Temperature
- Precision
- Pressure
- Chemical Compatibility
- Thermal Management
- Packaging
- Time to Prototype
- Scale
- Cost
- Integration of Components

Methods / Materials

Methods

- LIGA
- Wafer Processing (&DRIE)
- Soft Lithography
- Milling
- Laser Processing
- Electroforming
- ECM / EDM
- SFM
- Lamination (Bonding)
- Inkjet Deposition
- Screen Printing
- Polymer Fab
  - Injection Mold / Embossing

Materials

- Semiconductors
- Metals
- Polymers
- Ceramics
- Composites
- Glass

Materials

Ceramics

- Shrinkage (precision), porosity, brittle, interfacing

+ Access

Plastics

- Inertness, temperature, CTE, strength, precision(relative to ceramics)

+ Cost@volume, optics

Metals

- Precision in conventional machining

+ Material property knowledge base, cost, access, thermal, toughness

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Materials (con't.)

Semiconductors

- Defaulted to Schmidt presentation

+ Defaulted to Schmidt presentation

Glass

- Micromachining methods

+ Optics, temperature

Bonding

Need methods to laminate dissimilar materials

Recommendations - Materials

Bonding

- Methods to bond dissimilar materials

Glasses

- Good micromachining methods

Silicon

- Joining with other materials to capture electric properties

Recommendations - Materials (con't)

- Metals
  - Micromachining of bulk materials
- Plastics
  - Access to rapid prototyping (driven by BioMEMS?)
- Ceramics
  - Micromachining processes

Recommendations - Infrastructure

- Lamination (Bonding) is Omnipresent
- A foundry (perhaps virtual) which provides:
  - Micropatterned sheets of ceramic, silicon, metal, ...
  - Bonding methods
  - Standardized interfaces (fluidic and electric)
  - Design rules
- Standards - use the foundry
- Modeling - model the foundry process

Working Group III: Chemical Applications of Microchemical Systems

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- Definition
- Attributes
- Applications and Opportunities
- Shortcomings
- Research Needs
- Outlook
  - 3 years
  - 10 years
- Educational Needs

Definition of Microchemical Systems

- Systems with the following characteristics:
  - precisely controlled design
  - dimensions ranging from sub millimeters to sub micron
  - a chemical transformation takes place
  - scale-up is by replication

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Chemical Applications Working Group
ARO/DARPA *Workshop Microchemical Systems and Their Applications*

Attributes of Microreactors

- Integrated chemical production sensors, actuators
- Distributed - on demand - on time - in controlled quantities production
- Dual use: production of chemicals and information
- Portable, flexible, and smart devices
- Access to extreme operating conditions - Controlled conditions to novel compounds
- Safe operation (less inventory, ability to handle reactive, hazardous chemistry
- Fast non-equilibrium processes
- Short response times

Chemical Applications Working Group
ARO/DARPA *Workshop Microchemical Systems and Their Applications*

Attributes of Microreactors (continued)

- Efficient multiphase mass transfer (e.g., phase transfer catalysis)
- Simultaneous control of reaction and physical microstructure
  - formation and breaking of emulsions
  - crystallization
  - processing of colloids (incl nanoparticals)
- Use of forces associated with high surface to volume ratios
  - surface tension (control of bubble size, flow… .)
  - electroosmotic flows
- Large gradients for mass and heat transfer
- Laminar flow for separation, controlled mixing, fabrication

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Chemical Applications Working Group
ARO/DARPA *Workshop Microchemical Systems and Their Applications*

Examples of Current Applications

- DNA analysis
- Combinatorial chemistry
- Partial oxidation of alkanes
- Industry examples:
  - DuPont butyl-isocyanate synthesis
  - BASF vitamin
  - Merck (Germany) fine chemical
  - Aventis specialty polymers

Selected Applications Opportunities

- Personal chemistry devices
  - Diagnostics
  - Drug synthesis and delivery
  - Personal care and cosmetics
- Sustainable development - environmental friendly production
- Chemical production:
  - Fuels - reforming, upgrading, ...
  - Commodities and intermediates - HCN, phosgene, ...
  - Fine chemicals and pharmaceuticals - halogenation, nitration, oxidation, regioselectivity, ...
  - Biochemical - DNA analysis and synthesis, oligio sacharides, proteomics, cellular processes
- Discovery - pilot plant - efficient information collection - combinatorial approaches - statistically planned experimentation

Chemical Applications Working Group
ARO/DARPA *Workshop Microchemical Systems and Their Applications*

Potential Shortcomings

- ‘Sticky solids”- fouling
- Systems where high surface area to volume is a problem
  - surface adsorption, contamination, unintentional catalysis
- Low throughput per unit

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Research Needs

- Fundamental understanding
  - micromixing, fluid logic, surface chemistry and physical effects
  - when is the continuum approximation valid
  - transient behavior, chemical feedback, high gradients
  - interaction of electrostatic forces with chemistry and transport
  - patterning of surfaces (SAMS, soft lithography, …)
- Process modeling
  - surfaces, non-Newtonian flows, detailed chemistry, multiscale phenomena
- Systems analysis
  - when is smaller better - time, length, and energy scales
  - economics
- Control strategies
- Integration of micro sensors and actuators

Research Needs (Cont.)

- Packaging
  - materials
  - compatibility
  - interfaces - electronic & fluid handling
  - fabrication techniques
- Standards for integration and fabrication

Barriers and Challenges

- Bringing together multiple disciplines
- Infrastructure - fabrication foundries and engineering
- Exposure of technology to decision makers
- Intellectual property
- Packaging

Future Outlook - 3Years

- Integrated drug discovery
- Packaged, integrated, bench top laboratory tool
- Demonstrated production of chemicals in microchemical systems
- Combined chemical synthesis and analysis - SYNTAS
- Increased impact of microreaction technology on biomed.

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Opportunities - 3Years

- Decontamination chemistry
- Fogs and emulsions
- Portable fuel processing
- Potable water and air purification
- Personal medical devices
- BioChem detection
- Increased use in discovery and pilot plant
- Exponential growth in production of fine chemicals and production of test quantities

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Future Outlook - 10Years

- Exponentially decreasing cost of chemical information
- 10^3 types of microTAS
- 30% of fine chemicals produced by microchemical systems
- Personal chemistry - more chemical devices in the room than electronic today
- More modularity
- Microsystems available for particular reactions/chemistries
- Microsystems for materials synthesis (IT, ...)
- Small to medium size industrial base for microchemical systems

Educational Needs

- Interdisciplinary courses and modules
- Training of process personnel
- Short courses
- Handbook of microchemical systems

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